PB83-200238

Performance Test Results and Comparative Data for Designated Reference Methods for Nitrogen Dioxide

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring and Support Lab.
Research Triangle Park, NC

May 83

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/4-83-019
May 1983

PB83-200238

Performance Test Results and Comparative Data for Designated Reference Methods for Nitrogen Dioxide

by

Raymond M. Michie, Jr.
John A. Sokash
Betsy P. Fritschel
Environmental Quality Assurance Department
Research Triangle Institute
Research Triangle Park, NC 27709

Frank F. McElroy
Vinson L. Thompson
Methods Standardization Branch
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Contract Nos. 68-02-3222, 68-02-3431

EPA Project Officers: Frank F. McElroy, Vinson L. Thompson
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/4-83-019

2.

3. RECIPIENT'S ACCESSION NO.
PB83 200238

4. TITLE AND SUBTITLE
Performance Test Results and Comparative Data for
Designated Reference Methods for Nitrogen Dioxide

5. REPORT DATE
May 1983

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
R.M. Michie, Jr., J.A. Sokash, and B.P. Fritschel,
RTI, NC7 F.F. McElroy, V.L. Thompson, EPA

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Quality Assurance Department
Research Triangle Institute
Research Triangle Park, N.C. 27709

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
68-02-3222 and
68-02-3431

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in certain required monitoring. Such designation is based on performance testing of the analyzer model by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer, including performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the available EPA postdesignation test results for currently designated Nitrogen dioxide analyzers. Manufacturer's predesignation test results are presented for nine analyzers, and all test results met or exceeded the specifications. EPA postdesignation performance test results are presented for eight analyzers, and similarly, all test results met or exceeded the specifications. EPA postdesignation comparative test results are presented for nine analyzers, with the results indicating that the analyzers tested were stable and reliable and demonstrated a high degree of comparability.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
116

22. PRICE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for: assessing environmental monitoring technology and systems; implementing Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Assessment of environmental monitoring technology is performed in part by the Quality Assurance Division. Through the Equivalency Testing Program, automated analyzers are evaluated to ensure that explicit performance specifications are met. This document is one of four in a series that summarizes performance test results and comparative data obtained during analyzer evaluations. The series will document evaluations of analyzers that monitor ambient air for ozone, nitrogen dioxide, sulfur dioxide, and carbon monoxide.

ABSTRACT

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency designates specific ambient monitoring methods and analyzers as reference or equivalent methods acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring. Such designation requires that extensive performance testing of the analyzer be carried out by the manufacturer (or other applicant) prior to designation. After designation, EPA carries out further tests of the analyzer. These EPA tests include performance tests as well as comparative tests to evaluate the performance, reliability, and operational peculiarities of the analyzer with respect to other analyzers monitoring the same pollutant.

This report summarizes both the manufacturer's predesignation test results and the EPA postdesignation test results of the currently designated nitrogen dioxide analyzers. Manufacturer's predesignation test results are presented for ten analyzers. The manufacturer's tests were conducted according to procedures presented in 40 CFR Part 53, and all test results met or exceeded the specifications contained therein. EPA Phase I postdesignation test results are presented for eight analyzers. These tests were conducted according to an abridged version of the 40 CFR Part 53 procedures. Again, all test results met or exceeded the CFR specifications. EPA Phase II postdesignation test results are presented for nine analyzers. Although these tests were primarily comparative in nature with no formal performance specifications applicable to the data, the results indicated that the analyzers tested were stable, reliable, and demonstrated a high degree of comparability among themselves.

CONTENTS

Section **Page**

Foreword iii
Abstract iv
Figures. vi
Tables xi
Abbreviations and Symbols. xii
Acknowledgments. xiii

1 Introduction 1

2 Postdesignation Testing. 4

3 Test Results and Data for Designated Nitrogen Dioxide Analyzers 10
- Beckman 952A 13
- Bendix 8101B 23
- Bendix 8101C 27
- CSI 1600 41
- Meloy NA530R 49
- Monitor Labs 8440E 59
- Monitor Labs 8840. 68
- Philips PW9762/02. 77
- Thermo Electron 14 B/E 80
- Thermo Electron 14 D/E 90

Appendix A. Measurement Principle for NO_2 Analyzers 99

FIGURES

Number		Page
1	Beckman Model 952A NO/NO_2/NO_x Analyzer	13
2	Typical calibration curve for the Beckman 952A response . .	15
3	Zero and span drift in the Beckman 952A NO_2 readings during the Phase II ambient monitoring test	16
4	Correlation between the Beckman 952A and the average of the other analyzers during the Phase II ambient monitoring test	17
5	Frequency distribution of differences in hourly NO_2 ambient air readings between the Beckman 952A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected). . .	18
6	Frequency distribution of differences in hourly NO_2 ambient air readings between the Beckman 952A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected). .	19
7	Bendix 8101B Oxides of Nitrogen Analyzer	23
8	Bendix Model 8101C Oxides of Nitrogen Analyzer	27
9	Typical calibration curve for the Bendix 8101C NO_2 response	29
10	Zero and span drift in the Bendix 8101C NO_2 readings during the Phase II ambient monitoring test	30
11	Correlation between the Bendix 8101C and the average of the other analyzers during the Phase II ambient monitoring test	31
12	Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected). . .	32
13	Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected). .	33

FIGURES (continued)

Number Page

14 Zero and span drift in the Bendix 8101C (collocated) NO$_2$ readings during the Phase II ambient monitoring test . . 36

15 Correlation between the Bendix 8101C and the average of the other analyzers during the Phase II ambient monitoring test 37

16 Frequency distribution of differences in hourly NO$_2$ ambient air readings between the Bendix 8101C (collocated) and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test 38

17 Correlation between the Bendix 8101C (collocated) and the Bendix 8101C (original) during the Phase II ambient monitoring test 39

18 Frequency distribution of differences in hourly NO$_2$ ambient air readings between the Bendix 8101C (collocated) and the simultaneous readings from the Bendix 8101C (original) 40

19 CSI Model 1600 Oxides of Nitrogen Analyzer 41

20 Typical calibration curve for the CSI 1600 NO$_2$ response . . 43

21 Zero and span drift in the CSI 1600 NO$_2$ readings during the Phase II ambient monitoring test 44

22 Correlation between the CSI 1600 and the average of the other analyzers during the Phase II ambient monitoring test 45

23 Frequency distribution of differences in hourly NO$_2$ ambient air readings between the CSI 1600 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected). . . 46

24 Frequency distribution of differences in hourly NO$_2$ ambient air readings between the CSI 1600 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected). . 47

25 Meloy NA530R Nitrogen Oxides Analyzer 49

26 Typical calibration curve for the Meloy NA530R NO$_2$ response 52

FIGURES (continued)

Number Page

27 Zero and span drift in the Meloy NA530R NO_2 readings during the Phase II ambient monitoring test 53

28 Correlation between the Meloy NA530R and the average of the other analyzers during the Phase II ambient monitoring test 54

29 Frequency distribution of differences in hourly NO_2 ambient air readings between the Meloy NA530R and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected). . . 55

30 Frequency distribution of differences in hourly NO_2 ambient air readings between the Meloy NA530R and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected). . 56

31 Monitor Labs Model 8440E Nitrogen Oxides Analyzer 59

32 Typical calibration curve for the Monitor Labs 8440E NO_2 response 61

33 Zero and span drift in the Monitor Labs 8440E NO_2 readings during the Phase II ambient monitoring test 62

34 Correlation between the Monitor Labs 8440E and the average of the other analyzers during the Phase II ambient monitoring test 63

35 Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected). 64

36 Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected) 65

37 Monitor Labs Model 8840 Nitrogen Oxides Analyzer 68

38 Typical calibration curve for the Monitor Labs 8840 NO_2 response 71

39 Zero and span drift in the Monitor Labs 8840 NO_2 readings during the Phase II ambient monitoring test 72

FIGURES (continued)

Number Page

40 Correlation between the Monitor Labs 8840 and the average of the other analyzers during the Phase II ambient monitoring test 73

41 Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8840 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected) 74

42 Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8840 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected) 75

43 Philips Model PW9762/02 $NO/NO_2/NO_x$ Analyzer 77

44 Thermo Electron Model 14 B/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer 80

45 Typical calibration curve for the Thermo Electron 14 B/E NO_2 response 82

46 Zero and span drift in the Thermo Electron 14 B/E NO_2 readings during the Phase II ambient monitoring test 83

47 Correlation between the Thermo Electron 14 B/E and the average of the other analyzers during the Phase II ambient monitoring test 84

48 Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 B/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected) 85

49 Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 B/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected) 86

50 Thermo Electron Model 14 D/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer 90

51 Typical calibration curve for the Thermo Electron 14 D/E NO_2 response 92

FIGURES (continued)

Number Page

52 Zero and span drift in the Thermo Electron 14 D/E NO_2 reading during the Phase II ambient monitoring test 93

53 Correlation between the Thermo Electron 14 D/E and the average of the other analyzers during the Phase II ambient monitoring test 94

54 Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 D/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (corrected) 95

55 Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 D/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test (uncorrected) 96

TABLES

Number Page

1 Analyzers Included in the Phase II Testing of Nitrogen Dioxide Analyzers. 10

2 Estimates of Total Operating Precision and Minimum Detection Limits 12

3 Beckman 952A Laboratory Performance Test Results . . 14

4 Bendix 8101B Laboratory Performance Test Results . . 25

5 Bendix 8101C Laboratory Performance Test Results . . 28

6 CSI 1600 Laboratory Performance Test Results 42

7 Meloy NA530R Laboratory Performance Test Results . . 51

8 Monitor Labs 8440E Laboratory Performance Test Results 60

9 Monitor Labs 8840 Laboratory Performance Test Results. 70

10 Philips PW9762/02 Laboratory Performance Test Results. 78

11 TECO 14 B/E Laboratory Performance Test Results. . . 81

12 TECO 14 D/E Laboratory Performance Test Results. . . 91

ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm^3/min --cubic centimeter per minute
CFR --Code of Federal Regulations
DAMDF --Durham Air Monitoring Demonstration Facility
EMSL --Environmental Monitoring Systems Laboratory
EPA --U.S. Environmental Protection Agency
h --hour
Hz --hertz (frequency in cycles per second)
kPa --kilopascal
L --liter
LDL --lower detectable limit
mm --millimeter
MSB --Methods Standardization Branch
MDL --minimum detectable limit
NAMS --National Air Monitoring Station
NBS --National Bureau of Standards
PCB --printed circuit board
ppb --parts per billion
ppm --parts per million
PMT --photomultiplier tube
PSD --prevention of significant deterioration
psig --pounds per square inch, gauge
QAD --Quality Assurance Division
SLAMS --State and Local Air Monitoring Station
SRM --standard reference material
torr --unit of pressure (1 mm Hg @ 0° C or 133 N/m^2)
TFE --tetrafluoroethylene (Teflon)
µm --micrometer
URL --upper range limit
UV --ultraviolet
Vac --volts, alternating current

SYMBOLS

~ --approximately
CO --carbon monoxide
CO_2 --carbon dioxide
H_2O --water
H_2O(v) --water vapor
NO --nitric oxide
NO_x --oxides of nitrogen
NO_2 --nitrogen dioxide
O_3 --ozone
SO_2 --sulfur dioxide

ACKNOWLEGMENT

The authors gratefully acknowledge the invaluable statistical assistance of Mr. David Holland of the Data Management and Analysis Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency.

SECTION 1

INTRODUCTION

Under Part 53 of Title 40 of the Code of Federal Regulations (40 CFR Part 53), the U.S. Environmental Protection Agency (EPA) designates specific ambient monitoring methods and analyzers as acceptable for use in National Air Monitoring Stations (NAMS), State and Local Air Monitoring Stations (SLAMS), and Prevention of Significant Deterioration (PSD) monitoring, among other monitoring applications. These methods are designated as reference methods or equivalent methods, depending on whether or not the method employs a particular measurement principle and calibration procedure specified for each pollutant in 40 CFR Part 50. A list of all currently designated methods is available from the Quality Assurance Division (QAD) or from the Quality Control Coordinator at any EPA Regional Office.

Commercial analyzer models are designated as reference or equivalent methods on the basis of an application submitted by the manufacturer (or other applicant). This application must show that a test analyzer representative of the analyzer model meets the following criteria:

1. It has been tested according to specific test procedures prescribed in 40 CFR Part 53;
2. It meets prescribed minimum performance specifications; and
3. It meets certain other requirements such as having a suitable calibration procedure and an adequate operating or instruction manual.

Any designated analyzer model should meet the requirements mentioned above. However, these analyzer models may differ considerably in design, features, reliability, measurement principle, ease of operation, and level of performance above the required minimum. These factors allow for intelligent selection of the best or most appropriate analyzer for a particular application.

The Methods Standardization Branch (MSB) of the Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, NC, is responsible for EPA's reference and equivalent method designation program for ambient air monitoring methods. In this capacity, MSB acquires performance data and other information on these methods, particularly on the various commercial analyzer models that have been designated as reference or equivalent methods.

To summarize this information and make it available to those who may find it beneficial in selecting analyzers, MSB, with the assistance of the Research Triangle Institute, has prepared this report on designated methods for nitrogen dioxide (NO_2). Other reports discuss designated methods for ozone, sulfur dioxide, and carbon monoxide.

The information presented in this report is derived from the following sources:

1. The predesignation test data submitted by the applicant,
2. Postdesignation tests conducted by MSB,
3. Reports or comments from analyzer users, and
4. Other pertinent information as needed.

The predesignation test data were extracted from the application for designation submitted by the applicant (usually the analyzer manufacturer) and were thus obtained from tests conducted at the applicant's own laboratory or test site. These tests must be conducted in accordance with the explicit test procedures specified in 40 CFR Part 53. Results must then be calculated and interpreted according to the prescribed specifications.

The postdesignation tests conducted by MSB are part of an ongoing postdesignation testing program and may include one or more of the following types:

1. Phase I tests are laboratory performance tests similar to the predesignation tests required by 40 CFR Part 53;
2. Phase II tests simulate actual use conditions and serve to intercompare designated methods; and
3. Phase III tests are special purpose tests for specific individual analyzers and are used when unique needs or circumstances arise.

Postdesignation test results are the major source of information in this report and are described in detail in Section 2. The tests were conducted either by Quality Assurance Division personnel or by a contractor, under QAD direction, who had no contractual or financial association with any commercial manufacturers of designated analyzers. Because of resource limitations, there may be substantial delays in completing the postdesignation tests of an analyzer model following its designation as a reference or equivalent method.

The information in this report is based on files maintained by MSB for each designated method. MSB encourages analyzer users to submit comments that might be of interest to others using or contemplating purchase of a designated analyzer. Such comments, particularly negative comments, are more valuable if they are accompanied by supporting data, records, or other documentation. Pertinent information from other sources, such as other EPA groups, testing laboratories, and manufacturers will also be included when available. Publication of an updated report will be considered whenever significant new information is available. Additional information on any aspect of the report may be obtained from MSB. The report is not intended to recommend or endorse any particular analyzer over others. MSB welcomes any comments on the usefulness of these reports or suggestions for improvement. Remarks may be mailed to the address on the title page, or made by phone to any of the following numbers:

Commercial:	(919) 541-2622
	(919) 541-3791
FTS:	629-2622
	629-3791

SECTION 2

POSTDESIGNATION TESTING

Because the primary predesignation testing of an analyzer is carried out by the manufacturer or other applicant, it is EPA's general policy to perform followup performance tests on the analyzer after designation. These tests are referred to as postdesignation tests and are of three types: Phase I, Phase II, and Phase III. Phase I and II tests are described below. Phase III tests include any special tests or special circumstances not covered by Phase I and II and are conducted only when deemed necessary or appropriate.

The postdesignation tests are usually carried out on an analyzer purchased by EPA through normal procurement procedures after designation. Occasionally, an analyzer purchased prior to designation is returned to the manufacturer for upgrading to designated status. Commercially unavailable analyzers are borrowed for the tests. Prior to the tests, the manufacturer is informed of the impending test and that the test analyzer obtained will be assumed to be representative of the model. Because of the complex nature of most analyzers, variability in performance from one instrument to another can be expected. Even though all analyzers must be within the required specifications, this potential variability must be kept in mind when the test results in this report are considered and compared with those of other analyzers. Efforts were made during Phase II testing of NO_2 analyzers to quantify this variability by including two units from one of the manufacturers.

PHASE I TESTS

General Description

Phase I tests are laboratory performance tests that are conducted in accordance with the same test procedures and specifications required for the applicant's predesignation tests. The one exception is that fewer trials (usually four) are performed for each test parameter to reduce testing costs. All calibrations, test apparatus, pollutant standards, test procedures, test atmospheres, and test documentation are as specified in 40 CFR Part 53. An individual report containing more detailed information on the Phase I test for each analyzer tested is available from MSB.

Analyzers to be tested in Phase I are set up and allowed to operate for several weeks prior to actual testing. During this startup period, preliminary calibrations and linearity checks are performed to verify proper operation. In the event that unusual behavior such as nonlinearity or inoperability due to a major malfunction is identified, the manufacturer is notified. The manufacturer is encouraged to become involved throughout the startup period so that potential problems might be identified prior to testing. If a failure occurs during testing, the manufacturer is notified and given the opportunity to repair the analyzer. At the conclusion of the test, all failures and manufacturer involvement are documented and reported.

Data Interpretation

The Phase I test results for each analyzer are shown in Tables 3 through 12 along with the EPA performance specifications and the applicants' own predesignation test data (as submitted in the equivalency application). The results reported are averages of several trials for each parameter (usually four trials for the EPA Phase I data and seven for the applicant's predesignation data). The test results must generally be less than (or within) the EPA performance specifications shown for an analyzer to achieve designation, and, except for the lower detectable limit, these results are comparable in a relative sense from one instrument to another. The manufacturer's advertised or claimed performance specifications, however, may not be directly comparable to the test data or to other analyzers since manufacturers may choose to define their performance specifications, or how they are measured, differently. The various EPA performance parameters are described briefly below along with pertinent comments. See 40 CFR Part 53 for the formal definitions of the performance parameters and the prescribed test procedure for each.

Noise--

Noise refers to short-term deviations in the analyzer output that are not caused by changes in the input concentration. Noise is measured at both 0 percent and 80 percent of the upper range limit (URL) and is the standard deviation of 25 readings taken at 2-min intervals. Normally, this value will be slightly less than the average absolute deviation from the mean value and is usually much less than the peak-to-peak noise.

Lower Detectable Limit--

The lower detectable limit (LDL) is the smallest pollutant concentration that produces an output change of at least twice the noise level. The test does not determine the actual LDL; it only verifies that the output signal at an input concentration of 0.01 ppm is at least two times the 0-ppm noise level. Therefore, the value reported is usually close to 0.01 ppm and must be greater than twice the noise level. An output signal significantly lower than 0.01 ppm may indicate a nonapparent negative zero offset or other low level response problems.

Interference Equivalent--

The interference equivalent is the relative degree of unwanted response caused by compounds other than nitrogen dioxide present in the ambient air sample. The reported values should not be interpreted as the actual error to be expected in ambient measurements because the test concentrations of most of the interferents are higher than those normally encountered in ambient air. However, the values for water and carbon dioxide (CO_2) do represent the approximate error that may result when the calibration gases are dry and/or free of CO_2.

Zero Drift (12 h)--

The 12-h zero drift is the maximum change in continuous output response to zero input concentration over a 12-h period of unadjusted operation. The 12-h zero drift includes any peak-to-peak noise component so it may be higher than the 24-h zero drift.

Zero Drift (24-h)--

The 24-h zero drift is the net change in response to zero input concentration between two points in time ~24 h apart during unadjusted analyzer operation. It includes changes in ambient temperature, line voltage, or both. The 24-h zero drift tends to be positive sometimes and negative at others; hence the average would be misleadingly low. Therefore, the average of the absolute values of the analyzer's daily drift is reported in Tables 3 through 12 as a more meaningful value.

Span Drift (20% URL)--

The span drift at 20 percent URL is the net change in response to an input concentration of ~20 percent of the URL between two points in time ~24 h apart, during unadjusted analyzer operation and including changes in ambient temperature, line voltage, or both. Because the test procedure specifies no correction for zero drift, the reported value represents a combination of both zero drift and span drift over the period. The average of the absolute values is reported.

Span Drift (80% URL)--

The span drift at 80 percent URL is the net change in response to an input concentration of ~80 percent of URL between two points in time ~24 h apart, during unadjusted analyzer operation and including changes in ambient temperature, line voltage, or both. The 80-percent URL span drift is also calculated without a correction for zero drift; therefore it may be higher or lower than the actual change in the slope of the calibration curve. Again, the average of the absolute values of the individual daily results is reported.

Lag Time--

Lag time is the time required to observe the first change in response due to a sudden change in input concentration.

Rise Time--

Rise time is the time (not including the lag time) required for the response to reach 95 percent of its final value after a sudden increase in the input concentration.

Fall Time--

Fall time is the time (not including lag time) required for the response to decrease to 5 percent of its previous value when the input concentration is suddenly changed to 0 ppm.

Long lag, rise, or fall times generally do not adversely affect measurements expressed as hourly averages and may even be beneficial where concentrations fluctuate rapidly. However, long response times may be an annoyance or source of error during calibration and zero and span drift adjustment.

Precision--

Precision is the variation in the response value to six repeated measurements of the same upscale pollutant concentration, approached alternatively from lower and higher concentrations. The reported precision is a measure of the repeatability of the analyzer and is determined at both 20 percent and 80 percent of the URL.

PHASE II TESTS

General Description

Phase II tests are intended to test analyzers in a more or less typical ambient monitoring configuration where their stability, reliability, general performance, and operational peculiarities can be observed, recorded, and compared. The tests are conducted simultaneously on a group of analyzers during a period of several months. All analyzers measure the same pollutant in the ambient air, which is sampled from a common manifold. The ambient pollutant concentrations are sometimes augmented in the manifold with artificially generated pollutant to increase the concentration readings.

Unless otherwise specified, the Phase II tests are carried out at EPA's Durham Air Monitoring Demonstration Facility (DAMDF) in an urban/industrial/commercial area of Durham, NC. Ambient air samples for the analyzers are drawn from an intake on the building roof and distributed by an all-glass, power-ventilated manifold system. Pollutant levels are augmented, when appropriate. During such augmentation, however, all sample air contains at least 90 percent unaltered ambient air. The analyzers' inlets are connected to the manifold via Teflon® particulate filters and either 3-mm (1/8-in) or 6-mm (1/4-in) Teflon® tubing, depending on the analyzer flow rate. The sample lines are kept as short as practical.

All test analyzers are installed, calibrated, operated, and maintained in accordance with the manufacturer's operation/instruction manual and good monitoring practice. Analyzers receive a multipoint calibration initially and once per month during the test period. Two point zero and span checks are made two or three times per week, with zero adjustments only if the zero response is not within ±3 percent of full-scale response from nominal, and span adjustments only if the span (slope of calibration curve) changes by more than ±7 percent from nominal.

Zero air is obtained from filtered ambient air by appropriate drying and chemical scrubbing. Calibration and span gases are obtained by techniques such as dilution of high concentration cylinder gases, permeation devices, and gas phase titration. Ozone (O_3) concentrations are generated by ultraviolet (UV) radiation and are traceable to a UV standard; all other pollutant concentrations are traceable to National Bureau of Standards Standard Reference Materials (NBS-SRMs).

Analyzer readings are recorded at 1-min intervals using a Monitor Labs 9300 data acquisition system. One-hour averages (50 min minimum) are automatically calculated and transferred to magnetic tape. Zero and span responses are also recorded on the tape. The tapes are read into a Hewlett-Packard 9845A Desk Top computer for verification, editing, corrections as necessary, and calculation of the various statistical comparisons.

Data Interpretation

Phase II testing is primarily intended to be comparative in nature. As such, the test does not require conformance to any formal performance specifications, and the analyzers neither "officially pass" nor "officially fail" the comparisons. The Phase II test results and other data are presented in Section 3 as a series of figures for each analyzer. The figures in each analyzer's series (Figures 2 through 6, for example) are discussed in their order of appearance. The first (Figure 2, for example) is a typical multipoint calibration curve for the analyzer, showing five or more points spaced over the full-scale range, calculated by least squares regression from the actual calibration response data. The span is normally adjusted to a slope of ~200 (scale percent/ppm) for a 0 to 0.5 ppm range. The correlation coefficient provides an empirical measure of the linear association between the analyzer response and the calibration concentrations.

The chronological records of the zero and span drift for each analyzer are shown next in the series of figures (Figure 3, for example). Zero drift is plotted in absolute units (ppm) and the span drift is plotted as the percent difference in the span slope from the nominal slope (not percent-of-scale change in an arbitrary span concentration). Both zero and span drifts are total accumulated drifts except where manual adjustments are explicitly indicated by diamonds situated on the x-axis. The drifts are referenced to the nominal intercept (0 percent of scale) and nominal slope (200) represented by the horizontal, dashed lines. Also shown are the nominal adjustment limits for zero (±3 percent of full scale or ±15 ppb) and span (±7 percent). All adjustments, whether made because nominal drift limits were exceeded or during routine calibrations, are indicated by the diamonds. It is often not possible to adjust the zero and span to the exact nominal values desired because of the nature of the controls. The drift plots are intended mainly for visual comparison among the various analyzers.

The statistics shown above each chart give (1) the total net drift over the entire test period, ignoring adjustments and resets; (2) the number of individual drift periods--i.e, periods between zero and span checks; (3) the average length of the drift periods in days; (4) the average absolute value of the drift for each period (i.e., ignoring the signs of the drifts); and (5) the standard deviation of the individual drifts over all drift periods. The marker at the right side of each chart illustrates a drift range of ±3 standard deviations.

The next figure (Figure 4, for example) is a scatter diagram comparing each subject analyzer measurement (corrected for zero and span drift) with the average of the corresponding measurements from the other analyzers during simultaneous, continuous monitoring of ambient air over approximately 150 days. The linear regression relationship estimated from the data (solid line) is shown along with a dashed line representing the ideal linear relationship (slope = 1, intercept = 0). The linear regression slope and intercept have been tested statistically to determine if they are significantly different from 1 and 0, respectively. In general, the regression slopes and intercepts are significantly different even though they approximate the ideal values because of the large number of points (N) used in the regression. Also shown is the sample correlation coefficient (r).

The additional dashed lines on the scatter diagram show statistical bounds that should include 90 percent of future analyzer measurements (Y) for any concentration (X) as measured by the average of the reference analyzers. This is a 95-percent confidence interval, based on the estimated linear regression and centered on the estimated regression line, applicable to 90 percent of future observations.*

The next figure (Figure 5, for example) presents another comparison of the differences in hourly ambient air readings between the subject analyzer and the average of simultaneous readings from other analyzers. Corrections for zero and span drifts are made before the data are compared. The comparison is shown in the form of a frequency distribution indicating both numerically and graphically the frequency (number of hours out of the total test period) of the occurrence of each discrepancy versus its magnitude and sign. Also given are the correlation coefficient, the mean difference (bias), the standard deviation of the differences (spread), and the number of absolute differences >20 ppb; all of these are statistics calculated with respect to the differences between the hourly readings of the subject analyzer and the average of the corresponding hourly readings from the other analyzers in the test group.

Last is a figure (Figure 6, for example) showing the same type of frequency distribution discussed above but without periodic zero and span corrections; all hourly averages for the subject analyzers are based on the original calibration curve. The reference data from the analyzers on which the comparison is based are still corrected for zero and span drift. Comparison of the data in corresponding sets of frequency distributions, particularly the mean difference and the standard deviation of the differences, illustrates the effect of making periodic zero and span corrections to ambient monitoring data. Usually, the agreement of the hourly readings (bias, spread, or both) is improved by the periodic zero and span adjustments, and the practice is generally recommended where possible.

---

*A more detailed description of this type of confidence interval can be found in Lieberman, G. J, and R. G. Miller, Simultaneous Tolerance Intervals in Regression, Biometrika, 50:155-168, 1963.

SECTION 3

TEST RESULTS AND DATA FOR DESIGNATED NITROGEN DIOXIDE ANALYZERS

This section contains summary information on Phase I and Phase II postdesignation tests performed on nine nitrogen dioxide analyzers and predesignation test data for the other two designated NO_2 analyzers as reported by the instrument manufacturers in their applications for designation (see Table 1). The latter two analyzers have not undergone any postdesignation testing, nor is any anticipated as of this writing.

TEST RESULTS

Tables 3 through 12 summarize the available Phase I laboratory performance test results for each analyzer and compare these data with EPA specifications and with the manufacturer's predesignation test results. Phase II test results for each tested analyzer are shown in a series of figures con-

TABLE 1. ANALYZERS INCLUDED IN THE POSTDESIGNATION TESTING OF NITROGEN DIOXIDE ANALYZERS

Manufacturer	Model No.	Serial No.	Phase I tests	Phase II tests
Beckman	952A	1000013	Jul 79-Dec. 80	Apr-Sep 81
Bendix	8101B	---	No postdesignation testing anticipated	
Bendix (#1)	8101C	54974-281	Feb-Apr. 80	Apr-Sep 81
Bendix (#2)	8101C	Y00155-196	NA	Jun-Sep 81
CSI	1600	8853	Mar-Sep 80	Apr-Sep 81
Meloy	NA530R	8G091	Jul-79-Sep 80	Jun-Sep 81
Monitor Labs	8440E	125	May-Oct 80	June-Sep 81
Monitor Labs	8840	63	Jun-Oct 80	Apr-Jul 81
Philips	PW9762/02	---	No postdesignation testing anticipated	
Thermo Electron	14 B/E	AAM-0010	May, 80-Jan, 81	Apr-Sep 81
Thermo Electron	14 D/E	ADM/E 8788-102	Feb-Apr, 80	Apr-Sep 81

NA = Not applicable.

tained in each analyzer subsection. See Section 2 for an explanation of the tests and figures.

Determination of Minimum Detection Limit (MDL)

Of particular interest for any air monitoring analyzer is its minimum measurement capability. MDL can be defined as the lowest concentration that an analyzer can reliably distinguish from zero concentration. Note that this MDL is very similar to the lower detectable limit defined in 40 CFR Part 53 and discussed in Section 2. However, the test for LDL does not actually measure the LDL, it only determines that the LDL is greater than twice the noise level. In this study, an estimate of the MDL for each analyzer was determined by the following equation:

$$\text{MDL} = 3 \times \text{precision},$$

where the value 3 is the minimum recommended by the "Guidelines for Data Acquisition and Data Qaulity Evaluation in Environmental Chemistry"* and implies a risk of about 7 percent for concluding that a detectable concentration of NO_2 is present when the concentration is actually zero.

Rather than use the precision defined in 40 CFR Part 53 and measured in laboratory tests (Section 2) to estimate MDL, a more appropriate "total operating precision" of an analyzer was obtained from the Phase II test data. The total operating precision consists of the variance of two unpredictable, random sources of measurement error--the method precision and random bias. Random bias is caused by interfering substances that influence the ability of an analyzer to measure NO_2. The total operating precision is the square root of the sum of these two variance components.

The measurement of these components is relatively straightforward when there is a defined reference method measuring the "true" concentration or when replicate measurements are obtained. If neither reference method nor replicate measurements are available, total operating precision can be estimated by using principal component estimates as described by Lawton et al.† Using this procedure, estimates of total operating precision and corresponding estimates of MDL for each of the analyzers tested were made and are shown in Table 2.

This study included two Bendix 8101C analyzers. The readings from these two similar analyzers can be considered replicate measurements and thus provide an opportunity to estimate the precision of the 8101C by the more conventional process of dividing the standard deviation of the differences by $\sqrt{2}$.‡ With this procedure, the estimate of precision for the

---

*Analytical Chemistry, 52:2242, December 1980.

†Lawton, W. H., E. A. Sylvestre, and B. J. Young-Ferraro, Statistical comparison of multiple analytic procedures: Application of clinical chemistry, Technometrics, 21:397-409, 1979.

‡Youden, W. J., and E. H. Steiner, Statistical Manual of the Association of Official Analytical Chemists, Washington, D.C., 1975, page 23.

TABLE 2. ESTIMATES OF TOTAL OPERATING PRECISION AND MINIMUM DETECTION LIMITS

Analyzer	Total operating precision (ppm)	Minimum detection limit (ppm)
Beckman 952A	.0029	.0087
Bendix 8101C	.0019	.0057
Bendix 8101C (COL)	.0019	.0057
CSI 1600	.0020	.0060
Meloy NA530R	.0042	.0126
Monitor Labs 8440E	.0031	.0093
Monitor Labs 8840	.0041	.0123
Thermo Electron 14 B/E	.0018	.0054
Thermo Electron 14 D/E	.0030	.0090

Bendix analyzer was 0.0019, which agrees with the principal component estimates of 0.0019 shown in Table 2 for the 8101C.

It should be noted that these estimates of precision and MDL do not include errors associated with other operators and laboratories. Thus, these estimates are probably lower than would be determined if other variables were included.

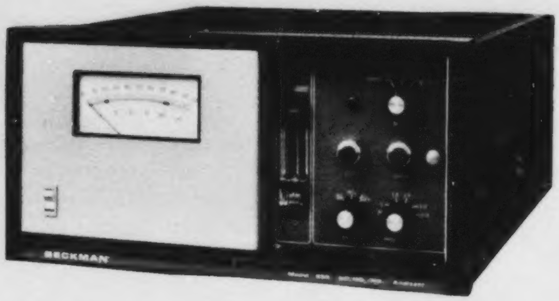


Figure 1. Beckman Model 952A NO/NO_2/NO_x Analyzer (RNA-0179-034).
Beckman Instruments, Inc., Process Instruments
Division, 2500 Harbor Boulevard, Fullerton, CA 92634

General Description

The Beckman 952A NO/NO_2/NO_x Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of nitric oxide (NO) and O_3 to form NO_2 as described in Appendix A. It is equipped with a single photomultiplier tube (PMT) and reaction chamber. The input sample stream is alternately routed around the NO_2-to-NO converter and through the converter to measure NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced within the analyzer by a UV lamp ozone generator. Single zero and span controls are provided, affecting all three output channels collectively.

To be used as a reference analyzer, the Model 952A must be operated on the 0 to 0.5 ppm range with the supplied 5-micrometer Teflon® filter installed in the sample inlet line. It may be operated with or without the Remote Operation option. The ambient temperature surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be in the range of 105 to 125 Vac, inclusive.

Table 3. Beckman 952A Laboratory Performance Test Results

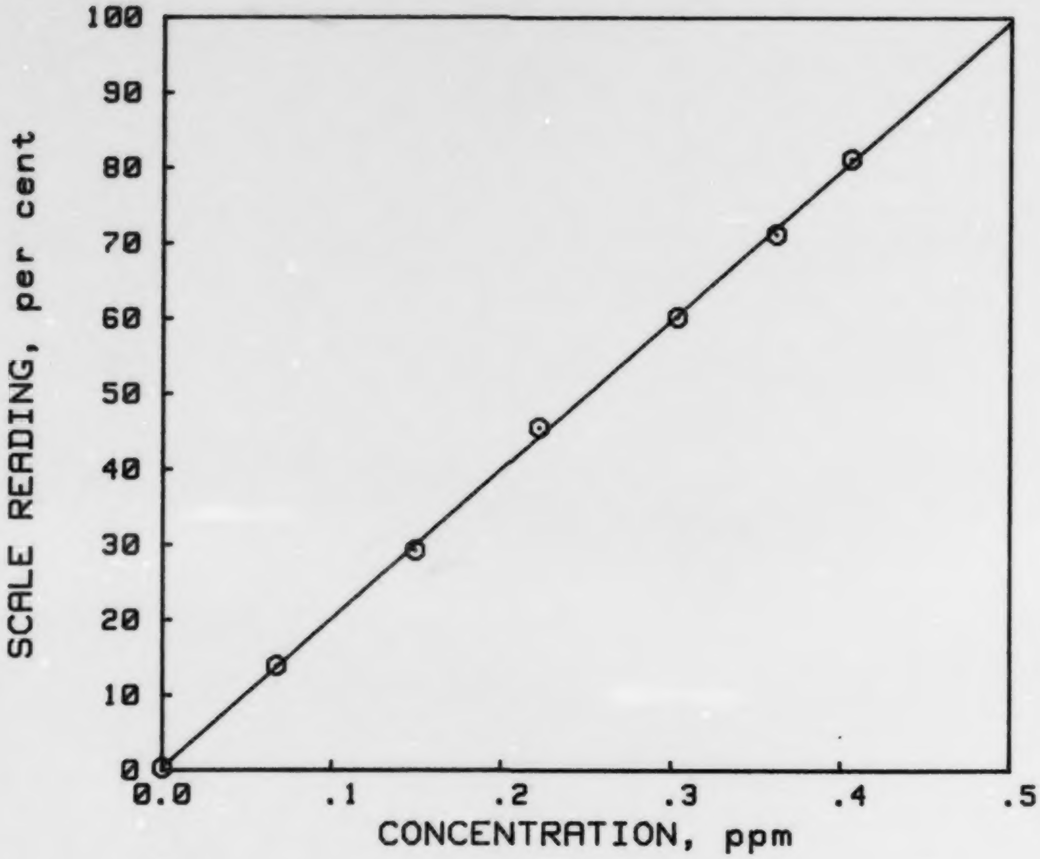
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.001
Noise – 80% URL	ppm	0.005	0.002	0.004
Lower detectable limit	ppm	0.01	0.008	0.010
Interferents	ppm			
SO_2		±0.02	<-0.001	0.001
NO		±0.02	<0.001	-0.012
NH_3		±0.02	0.000	0.000
H_2O		±0.02	0.000	-0.002
Total interferents		≤0.04	0.003	0.014
Zero drift – 12 h	ppm	±0.02	0.008	0.006
Zero drift – 24 h	ppm	±0.02	0.001[d]	0.002[d]
Span drift – 20% URL	%	±20.0	3.31[d]	8.38[d]
Span drift – 80% URL	%	±5.0	0.86[d]	1.98[d]
Lag time	min	20	0.5	1.0
Rise time	min	15	1.5	0.4
Fall time	min	15	1.0	0.6
Precision – 20% URL	ppm	0.020	0.001	<0.001
Precision – 80% URL	ppm	0.030	0.001	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 1000013.

[d] Average of absolute values.



ANALYZER: BECKMAN
MODEL: 952A
SERIAL No.: 1000013
POLLUTANT: NO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 06/05/81
DATE CODE: 81.156
NAME: RTI

Y = MX + A

M = 198.214
95% C.I.= ± 5.317

A = .361
95% C.I.= ± 1.360

r = .99973

DATA:	X	Y
1	0.000	.234
2	.067	13.897
3	.149	29.214
4	.222	45.560
5	.303	60.270
6	.362	71.260
7	.406	81.260

Figure 2. Typical calibration curve for the Beckman 952A response.

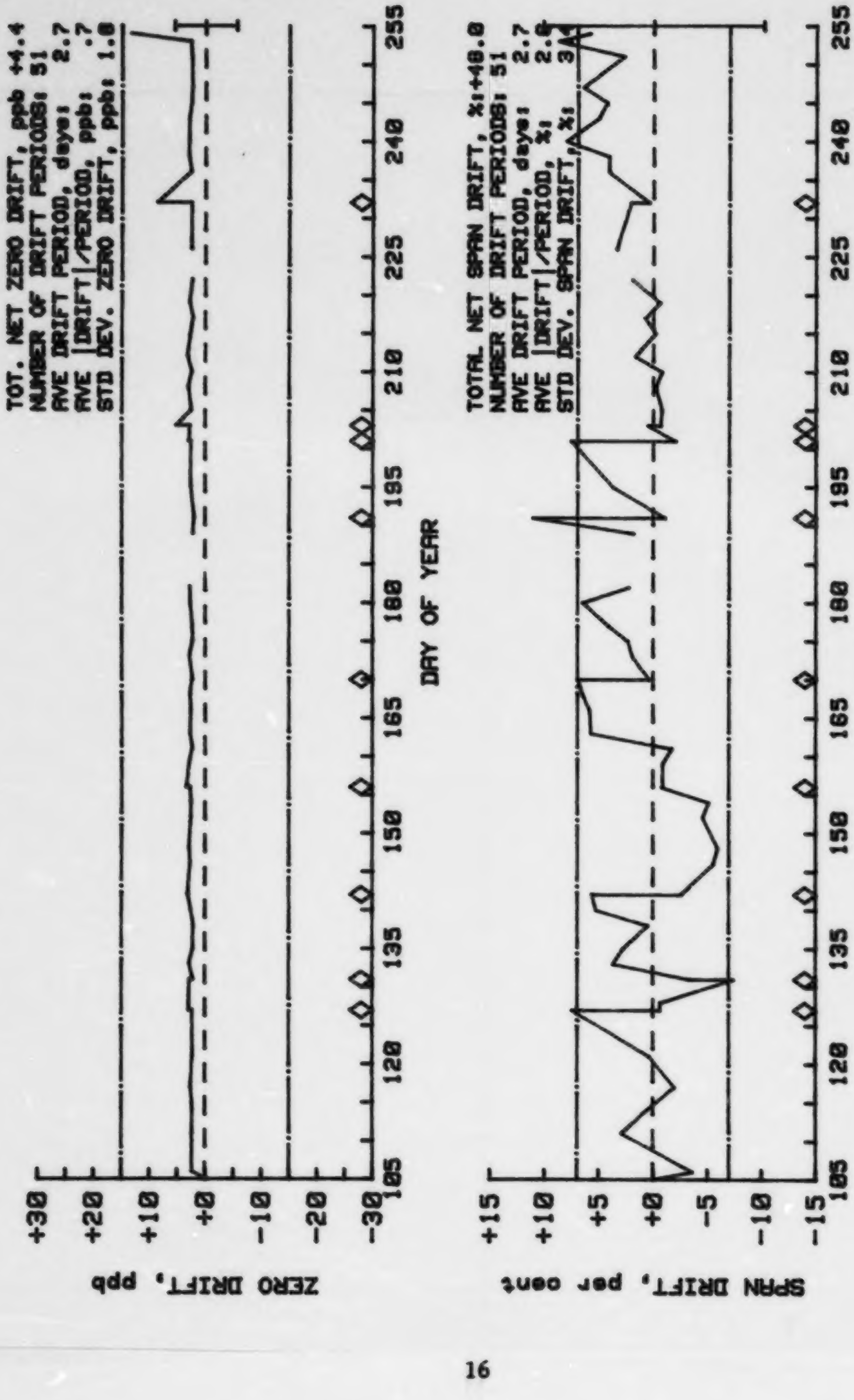


Figure 3. Zero and span drift in the Beckman 952A NO_2 readings during the Phase II ambient monitoring test.

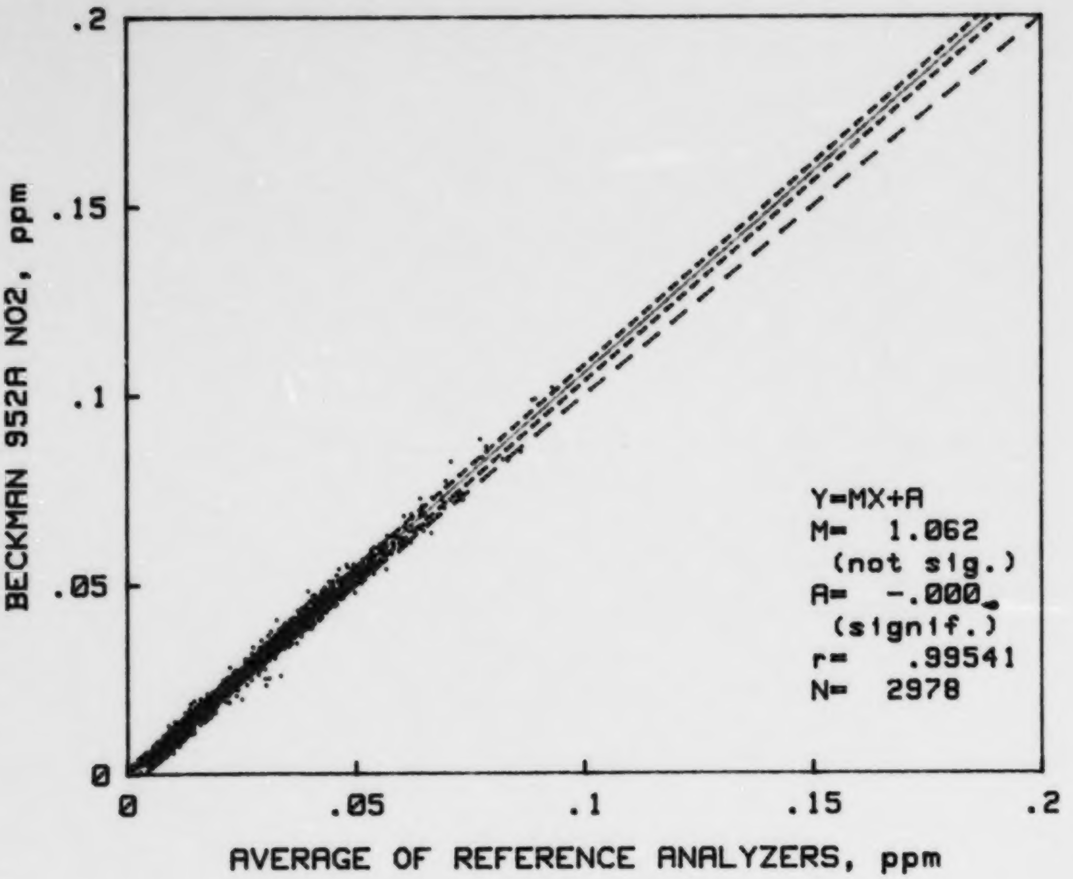
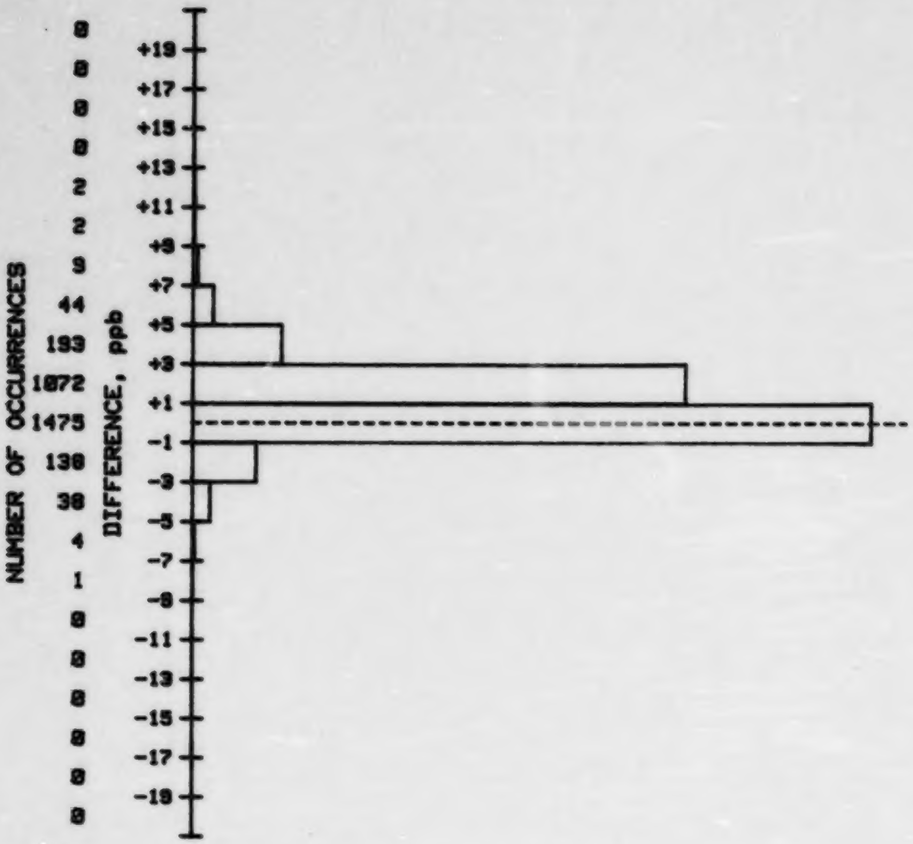


Figure 4. Correlation between the Beckman 952A and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BECKMAN 952A NO2

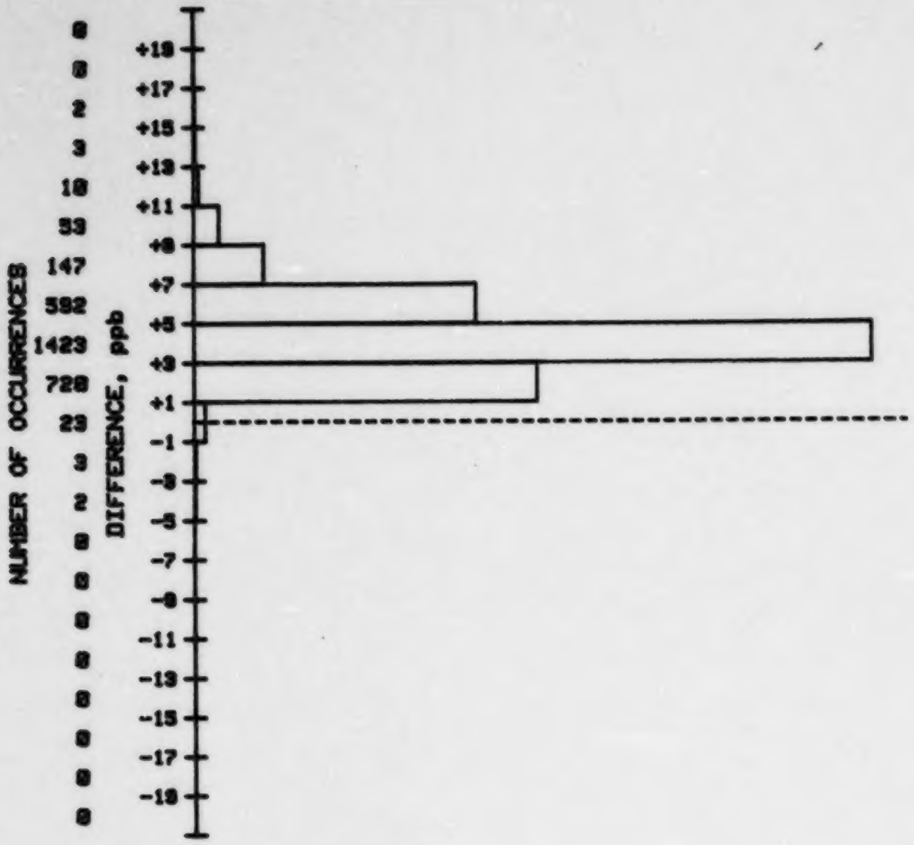


TOTAL No. OF DATA PAIRS: 2978
CORRELATION COEFFICIENT: .995407
MEAN DIFFERENCE, ppb: +.97
STD. DEVIATION OF DIFFERENCES, ppb: 1.5932
MAX. ABSOLUTE DIFFERENCE, ppb: 12
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 5. Frequency distribution of differences in hourly NO_2 ambient air readings between the Beckman 952A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BECKMAN 952A NO2



TOTAL No. OF DATA PAIRS: 2978
CORRELATION COEFFICIENT: .994410
MEAN DIFFERENCE, ppb: +4.21
STD. DEVIATION OF DIFFERENCES, ppb: 1.8347
MAX. ABSOLUTE DIFFERENCE, ppb: 16
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 6. Frequency distribution of differences in hourly NO_2 ambient air readings between the Beckman 952A and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Beckman readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample inlet filter element	Monthly
Check converter efficiency	Monthly
Perform internal leak check procedure	Monthly
Perform sample pump checkout procedure	Monthly
Check NO/NO_x flow balance	Monthly
Replace ozone-air scrubber	Semiannually

Malfunctions

During the postdesignation testing of this analyzer, the time required for adjustment, troubleshooting, and repair activities was significant with respect to the overall test period. Additionally, the quantity of replacement parts required for continued operation was not trivial. The repair time and replacement parts requirements far exceeded those typically experienced for six of the eight similar analyzers evaluated during this testing. A total of 19 parts were replaced during the Phase I and Phase II testing periods. Typical part requirements for similar analyzers in the project ranged from zero to four replacements during the test period. The parts required on the Model 952A were:

- NO_2-to-NO converter heating mantle,
- NO_2-to-NO converter (three different replacements),
- Cooling fan,
- Sample pump (three different replacements),
- Converter-temperature-monitoring thermistor,
- Sample back pressure regulator,
- Ozone generator,
- Ozone generator air supply scrubber,
- PMT cooler and housing,
- PMT cooler fuse,
- R5 on the PMT cooler control PCB,
- Primary amplifier PCB,
- Solenoid inlet filter and fitting,
- Converter bypass capillary, and
- Sample pump diaphragms.

During Phase I testing, an estimated 36 days were required for troubleshooting or actual repairs and another 8 days were required for routine or nonroutine adjustments. Offsite service required 4 months. An estimated 6½ months of the 17-month Phase I test period were consumed in corrective maintenance activities, which amounts to 38 percent of the entire test period. During Phase II testing, however, corrective maintenance requirements dropped considerably to a level of 7 days in the 150-day test.

General Comments

Phase I testing was the first monitoring activity performed by this analyzer. It was received as a new analyzer from Beckman on December 6, 1978.

In March 1980, it was noted that unequal responses to NO atmospheres were being recorded from the NO and NO_x channels. The imbalance amounted to a 7-percent-of-scale greater response from the NO channel than from the NO_x channel. This problem persisted throughout Phase I testing and, as discussed below, was finally resolved during Phase II testing.

This analyzer is equipped with a single PMT, which alternately measures both NO and NO_x concentrations in the sample stream. The continuous output signal from the PMT is amplified by a single primary amplifier and then is passed on to separate NO and NO_x channel amplifiers on the Readout PCB. The single zero and span controls for the analyzer affect the operation of the amplifiers in the primary amplification section only. Internal adjustments of the zero for the NO, NO_2, and NO_x secondary amplifiers are provided; however, no span adjustments are provided for these amplifiers. Initially, it was believed that misadjustment of the secondary amplifiers was causing the imbalance problem. However, by monitoring the output signal at the output from the primary amplifier (before the secondary amplifiers), it was shown that the imbalance was actually being sensed by the PMT and was not a phenomenon of electronic misadjustment.

The routine startup procedure in the operating manual explicitly describes the balancing of flows between the NO and NO_x flow paths (see Section 3.3, part 7, in the operating manual). This procedure involves setting a specific flow through the NO_2-to-NO converter (the NO_x flow path), then matching this flow in the path around the converter (the NO flow path). A significant amount of effort was expended during this test to ascertain that the volumetric flow rate in each of these legs was, indeed, equal within 1 or 2 cm^3/min. Nevertheless, the output signal imbalance persisted. However, when the converter was removed from the NO_x leg (i.e., the converter was bypassed), the signal responses from the two channels became equal.

It was finally concluded that a slight pressure reduction was being induced in the NO_x leg by the converter itself. Based on conversations with Beckman representatives during Phase II testing in April 1981, a decision was made to modify the flow balance procedure described in the manual. The responses from the NO and NO_x channels to a NO span atmosphere were balanced by adjusting the flow in the NO leg as necessary. This eliminated the output signal imbalance problem by creating a slight imbalance in the flows in the two legs as measured by the analyzer's front panel rotameter.

In April 1980, the analyzer failed three of four 24-hour drift tests at 80 percent of full scale. Drift values of 6.7, -6.5, and 5.2 percent were obtained for tests conducted on Test Days 1, 3, and 4, respectively. A value of -2.6 percent was obtained on Test Day 2. These failures were attributed to the failure of the PMT cooler to adequately control PMT temperature during the test temperature cycles. Subsequent tests, conducted in October 1980 after repair of the damaged cooler, were successfully passed with an average 80-percent-of-scale drift of 1.7 percent.

Two apparent design inadequacies were noted during this test that are worth mentioning here. First, the charcoal scrubber used to remove residual ozone from the exhaust gas stream was designed to be placed downstream of the sample pump. The passage of high concentrations of ozone through the pump required that the pumping chamber be Teflon®-coated, the diaphragms be Teflon®-lined, and inlet/outlet fittings be stainless steel. These requirements increased both the cost and the maintenance requirements for the pump.

Second, certain required, routine electronic adjustments were made unnecessarily difficult by the placement of components within the analyzer. The routine calibration procedure described in the operating manual (Section 4.1.3) required the adjustment of potentiometer R4 on the high voltage PCB as part of the NO/NO_x channel's calibration. Adjustment of this potentiometer required removal of the analyzer cover even though the potentiometer can be seen through the front access door. The startup procedure (Section 3, part 4) required adjustment of three potentiometers on the primary amplifier PCB. Not only did the cover have to be removed from the analyzer to gain access to these adjustment points, but the analyzer had to be shut down completely and the Readout Board removed from the motherboard. After removal of the Readout Board, certain connections were reestablished, the analyzer turned on, and the adjustments made. After the adjustments were complete, the disassembly process (including analyzer shutdown) was reversed for reassembly. These procedures were unnecessarily complicated and time-consuming.

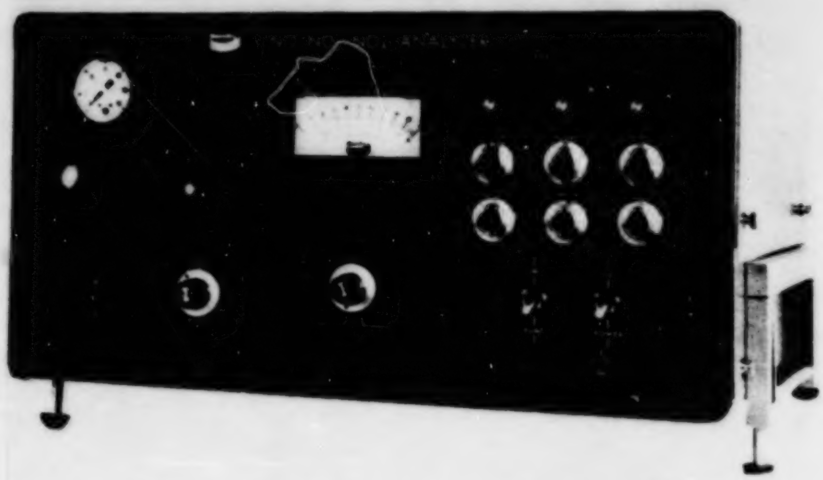


Figure 7. Bendix 8101B Oxides of Nitrogen Analyzer (RFNA-0479-038). The Bendix Corporation, Environmental and Process Instruments Division, P.O. Box 831, Lewisburg, WV 24901.

General Description

The Bendix 8101B Oxides of Nitrogen Analyzer has not been in production since it was replaced by the Model 8101C. But many Model 8101B analyzers are still in use and are covered by this reference method designation. Also, upgrading pre-8101B analyzer models to 8101B designated status is considerably less expensive than upgrading them to Model 8101C designated status.

As with the Model 8101C, this analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with a single photomultiplier tube and reaction chamber. The input sample stream is alternately routed around the NO_2-to-NO converter and through the converter to provide measurement of NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced within the analyzer by a high voltage discharge generator. The original design of this model required a source of compressed oxygen gas for ozone generation. Currently, an option is available that enables the analyzer to utilize ambient air as the ozone-generation source gas. It employs an on-board permeation drier for gas drying.

To be used as a reference analyzer, this model must undergo the following postmanufacture modifications:

1. Installation of the ozone generator and reaction chamber input-output tubing modification per Bendix Service Bulletin 8101B-2,
2. Installation of the approved converter material, and
3. Use of the revised and EPA-approved operation and service manual.

These modifications are mandatory and must be obtained from Bendix. Further, the analyzer must be operated on the 0-0.5 ppm range with a Teflon® filter installed in the sample inlet line. The following options may also be selected, if desired:

1. The Perma Pure® dryer/ambient air modification,
2. The valve cycle time modification,
3. The zero potentiometer centering modification per Bendix Service Bulletin 8101B-1, and
4. The reaction chamber vacuum gauge modification.

The ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 4. Bendix 8101B Laboratory Performance Test Results

Performance parameters	Units	EPA specs.[a]	EPA Predesignation test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	
Noise – 80% URL	ppm	0.005	0.002	
Lower detectable limit	ppm	0.01	0.005	
Interferents	ppm			
SO_2		±0.02	0.001	NO
NO		±0.02	−0.013	PHASE I
NH_3		±0.02	<0.001	TESTING
H_2O		±0.02	−0.008	ANTICIPATED
Total interferents		<0.04	0.021	
Zero drift – 12 h	ppm	±0.02	0.005	
Zero drift – 24 h	ppm	±0.02	<0.001[d]	
Span drift – 20% URL	%	±20.0	1.99[d]	
Span drift – 80% URL	%	±5.0	1.67[d]	
Lag time	min	20	0.5	
Rise time	min	15	1.0	
Fall time	min	15	1.0	
Precision – 20% URL	ppm	0.020	0.001	
Precision – 80% URL	ppm	0.030	0.003	

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from EPA tests conducted for equivalency determination; see General Comments.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample particulate filter	Monthly or when required
Replace exhaust filter charcoal	Bimonthly
Service vacuum pump	When required
Clean exterior and interior surfaces of instrument	When required
Replace NO_2-to-NO converter	When required
Replace oxygen filter	When required
Replace oxygen cylinder	When required

General Comments

As noted on page 24, the Bendix Model 8101B is no longer in production and was not in production at the time of designation. Because of the substantial number of 8101B units owned and used by EPA as well as many other units known to be in use in State and local agencies, EPA decided to conduct the necessary predesignation tests itself, as permitted under section 53.5 of 40 CFR Part 53. Accordingly, the test data appearing in Table 4 were obtained by EPA in predesignation tests. The designation, however, was made with the full cooperation and support of the Bendix Corporation and is considered a joint designation. No further postdesignation testing is planned.

BENDIX 8101C

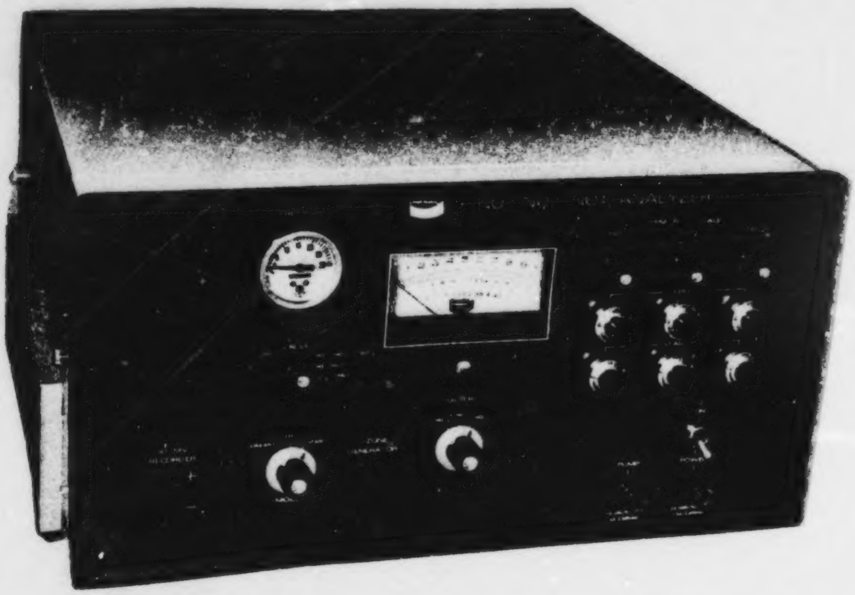


Figure 8. Bendix Model 8101C Oxides of Nitrogen Analyzer (RFNA-0777-022). The Bendix Corporation, Environmental and Process Instruments Division, P.O. Box 831, Lewisburg, WV 24901.

General Description

The Bendix 8101C Oxides of Nitrogen Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2, as described in Appendix A. It is equipped with a single photomultiplier tube and reaction chamber. The input sample stream is alternately routed around the NO_2-to-NO converter and through the converter to provide measurement of NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced within the analyzer by a high voltage discharge generator. Air for the ozone generator is dried within the analyzer by a permeation drier. Separate zero and span controls are provided for each of the three output channels (NO, NO_2, and NO_x).

To be used as a reference method, the Model 8101C must be operated on the 0 to 0.5 ppm range with a Teflon® sample filter installed in the inlet line. Ambient temperature surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be in the range of 105 to 125 Vac, inclusive.

Table 5. Bendix 8101C Laboratory Performance Test Results

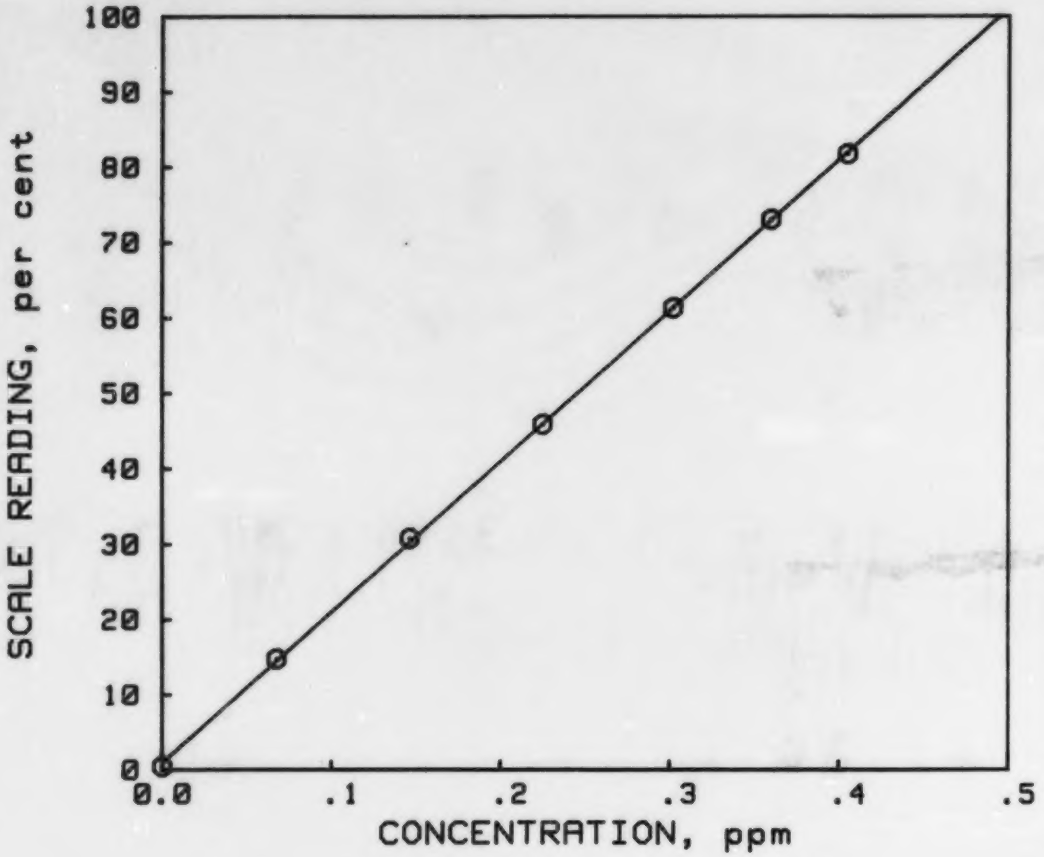
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	0.001
Noise – 80% URL	ppm	0.005	0.001	0.003
Lower detectable limit	ppm	0.01	0.011	0.009
Interferents	ppm			
SO_2		±0.02	0.000	0.001
NO		±0.02	0.004	-0.002
NH_3		±0.02	0.000	<-0.001
H_2O		±0.02	-0.007	-0.003
Total interferents		≤0.04	0.012	0.005
Zero drift – 12 h	ppm	±0.02	0.003	0.003
Zero drift – 24 h	ppm	±0.02	<0.001[d]	0.002[d]
Span drift – 20% URL	%	±20.0	2.10[d]	2.90[d]
Span drift – 80% URL	%	±5.0	1.42[d]	1.07[d]
Lag time	min	20	0.5	<1.0
Rise time	min	15	0.4	1.0
Fall time	min	15	0.8	<1.0
Precision – 20% URL	ppm	0.020	0.001	0.002
Precision – 80% URL	ppm	0.030	0.001	0.004

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 54974-281.

[d] Average of absolute values.



```
ANALYZER:     BENDIX          Y = MX + A        DATA:   X         Y
MODEL:        8101C                                    ----      ----
SERIAL No.:   54974-281       M =   200.368        1   0.000      .395
POLLUTANT:    NO2              95% C.I.= ± 2.628   2    .068    14.737
RANGE:         .5 ppm                              3    .146    30.772
LOCATION:     DAMDF           A =       .927       4    .225    45.890
DATE:         06/05/81         95% C.I.= ±  .674   5    .302    61.350
DATE CODE:    81.156                               6    .360    73.080
NAME:         RTI             r =    .99993        7    .405    81.760
```

Figure 9. Typical calibration curve for the Bendix 8101C NO_2 response.

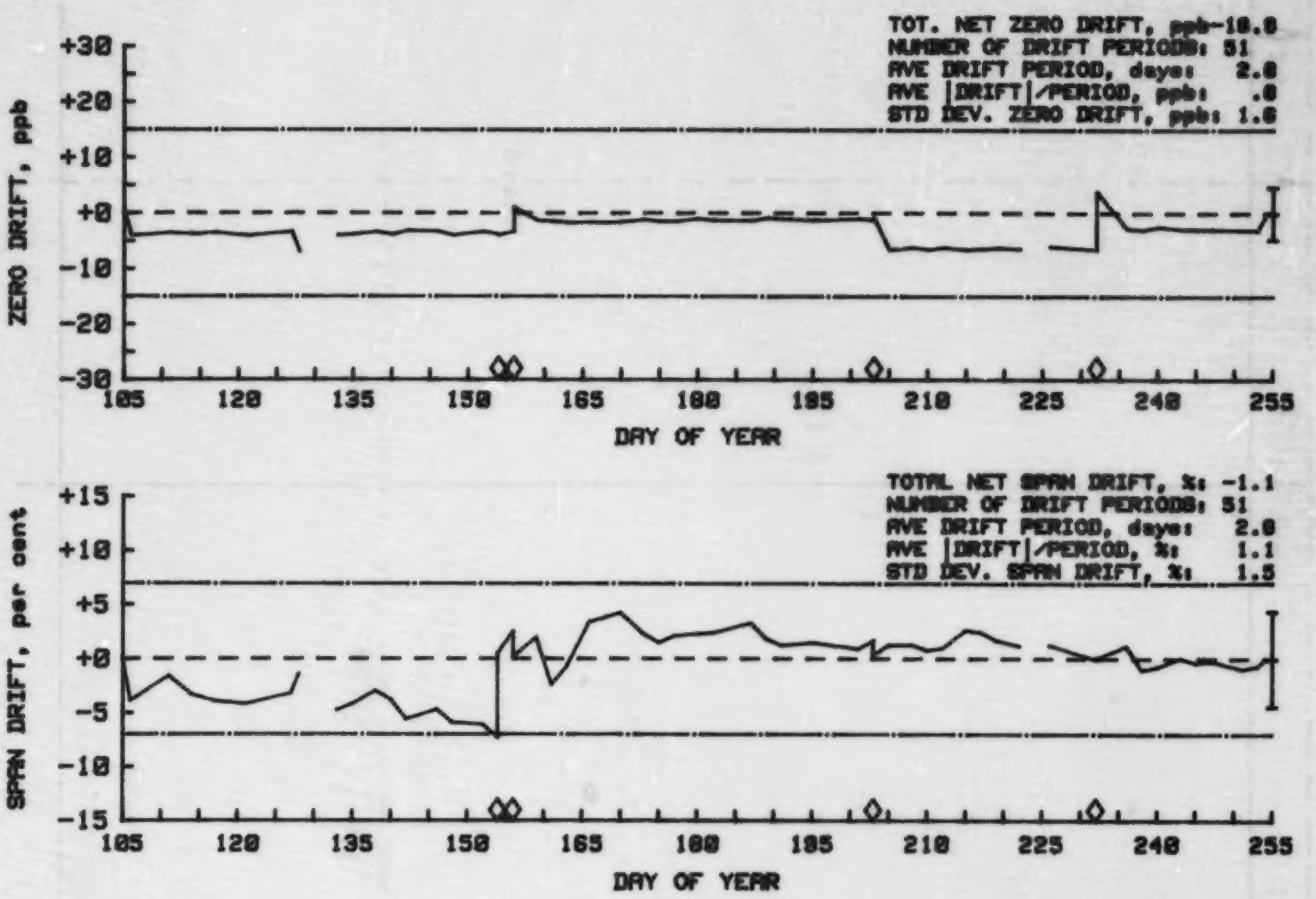


Figure 10. Zero and span drift in the Bendix 8101C NO_2 readings during the Phase II ambient monitoring test.

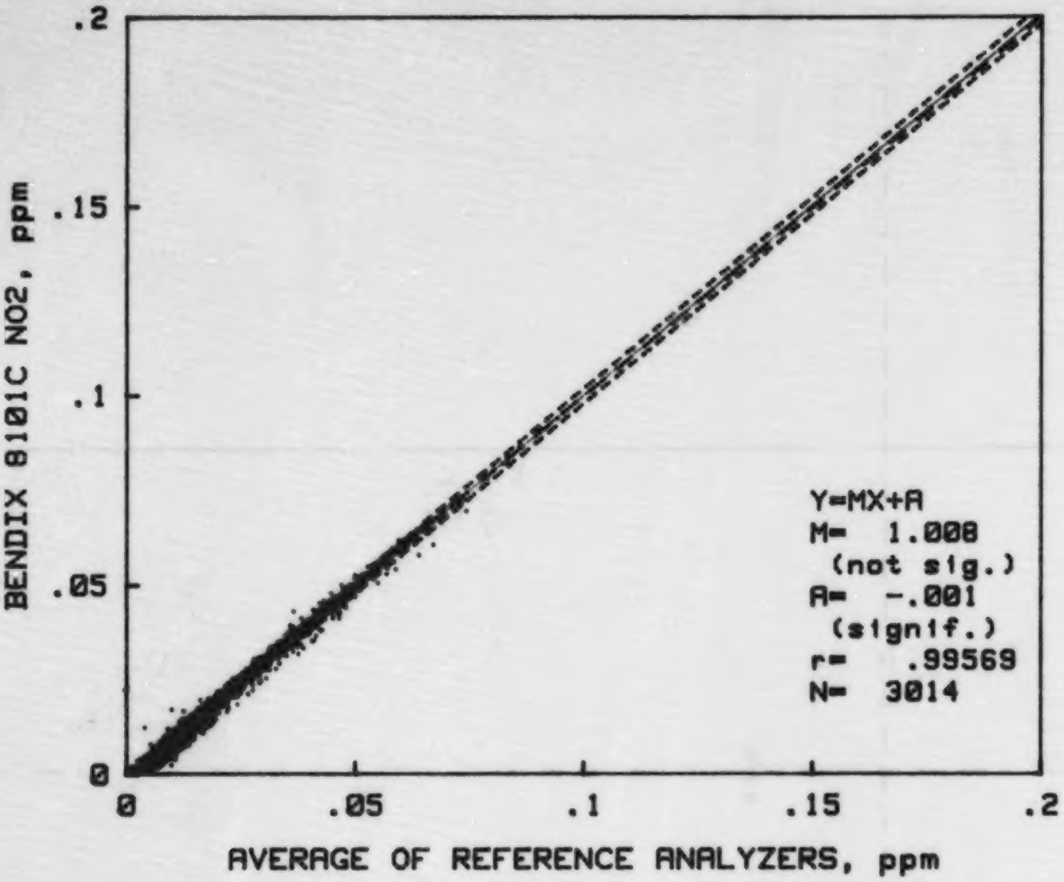
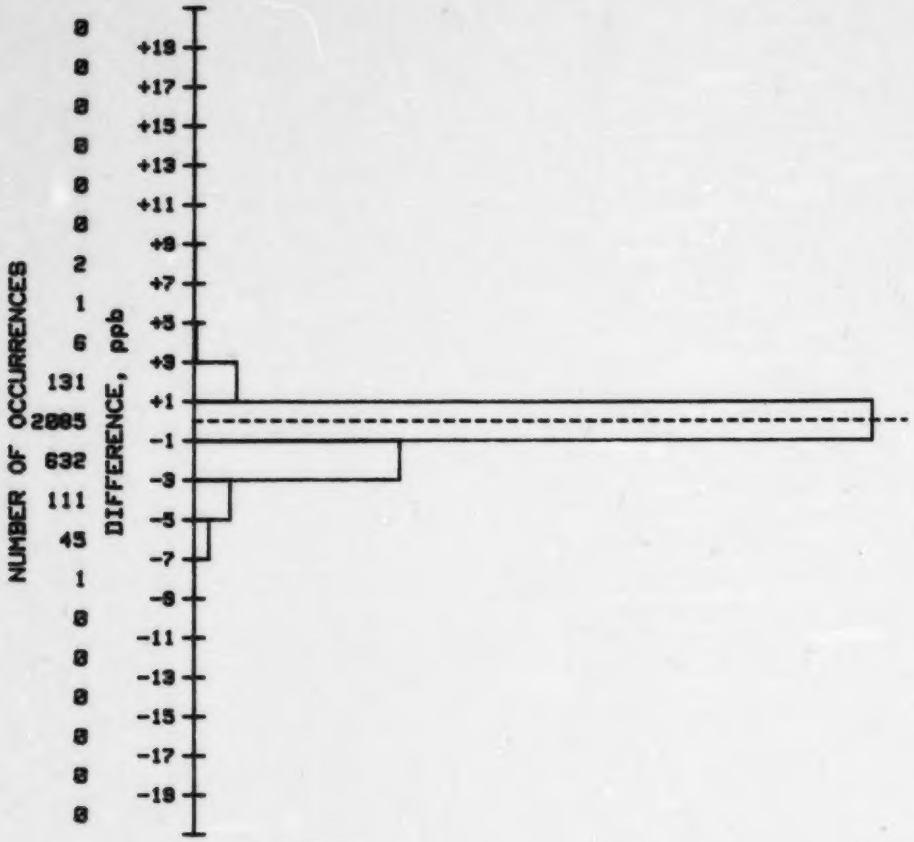


Figure 11. Correlation between the Bendix 8101C and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BENDIX 8101C NO2

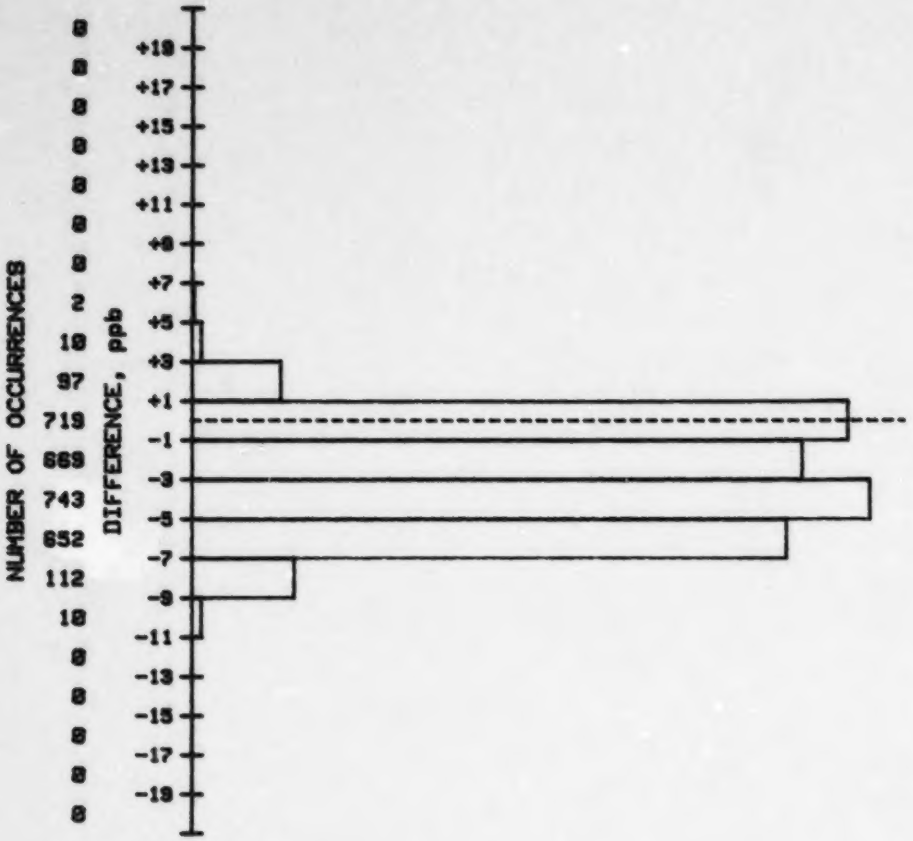


TOTAL No. OF DATA PAIRS:	3014
CORRELATION COEFFICIENT:	.995693
MEAN DIFFERENCE, ppb:	-.63
STD. DEVIATION OF DIFFERENCES, ppb:	1.2677
MAX. ABSOLUTE DIFFERENCE, ppb:	8
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 12. Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BENDIX 8101C NO2



```
TOTAL No. OF DATA PAIRS:                 3014
CORRELATION COEFFICIENT:                      .984186
MEAN DIFFERENCE, ppb:                   -3.06
STD. DEVIATION OF DIFFERENCES, ppb:    2.5074
MAX. ABSOLUTE DIFFERENCE, ppb:          11
NO. ABSOLUTE DIFFERENCES >20:            0
```

Figure 13. Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Bendix readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace sample particulate filter	Monthly or when required
Replace exhaust filter charcoal	Bimonthly
Service vacuum pump	When required
Clean exterior and interior surfaces of instrument	When required
Clean ozone generator	Every 3 months
Replace NO_2-to-NO converter	When required

Malfunctions

Throughout Phase I and Phase II testing, the solenoid valve switching the sample stream alternately through and around the NO_2-to-NO converter was replaced six times. The replacement dates and approximate service durations were:

Replacement date	Service life
7-79	Unknown
2-80	4½ months
4-80	2 months
3-81	8 months
4-81	3 days
4-81	12 days

It should be noted that some of the intervals between replacements included 2 to 4 months of analyzer nonoperation. For this reason, the replacement intervals do not necessarily correspond to the service intervals. The mode of valve failure was the same in all cases: the valve became mechanically "stuck" in the normally open position, thus allowing analyzer quantitation of NO but not NO_2. Since the failure was mechanical rather than electrical, the analyzer electronics continued to process the PMT output signal according to the routine, cyclic program, which produced normal output during the NO portion of the cycle and nearly identical output during the NO_x portion of the cycle. This output resulted in a zero response from the NO_2 channel at all times, whether or not NO_2 was present in the sample. The last replacement valve, installed in April 1981, operated until the end of Phase II testing in September 1981. The instruction manual for the analyzer makes no reference to the anticipated service life for the valve. Additionally, no routine maintenance is specified.

General Comments

With the exception of the failures of the sample solenoid valve, this analyzer was among the three most reliable and service-free analyzers tested during this program.

A second Bendix 8101C analyzer was added to the Phase II test group on May 22, 1982, to provide comparison data for collocated analyzers of the same make and model. The collocated analyzer operated without incident until the end of the test in September 1981 (115 days). Figures 14 through 18 present data derived from the collocated unit. Figure 14 presents the chronological records of zero and span drift for the analyzer. It may be interpreted in the same manner as the similar plots included for each of the other analyzers. Figure 15 is a scatter diagram comparing the collocated analyzer measurements of hourly ambient data (corrected for zero and span drift) with the average of the corresponding measurements from the other analyzers. The linear regression (least squares) relationship estimated from the data (solid line) is shown along with a dashed line representing the ideal linear relationship (see Section 2 for a more complete description of this type of figure). Figure 16 presents the frequency distribution of the differences in hourly ambient air readings between the collocated Model 8101C and the average simultaneous readings from all of the other analyzers. The distribution is presented both numerically and graphically. Figure 17 is similar to Figure 15 except that it is a plot comparing the measurements of the collocated analyzer with the original analyzer only. The regression statistics presented are based on an orthogonal analysis rather than a least-squares analysis. The orthogonal statistics* are similar to ordinary least-squares regression statistics. However, least-squares regression assumes that one of the variables is dependent on the other variable, that the independent variable has zero measurement error, and that all of the variance (scatter) in the data points must be due to the variance in the dependent variable. Since this is not the case when comparing two independent analyzers, the balanced orthogonal analysis, which assumes equal measurement error in both variables, has been used. Figure 18 presents the frequency distribution of differences in hourly ambient air readings between the collocated Model 8101C and the original Model 8101C alone.

---

*Manansky, A., The Fitting of Straight Lines When Both Variables are Subject to Error, J. Am. Stat. Assoc., 54:173-205, 1959.

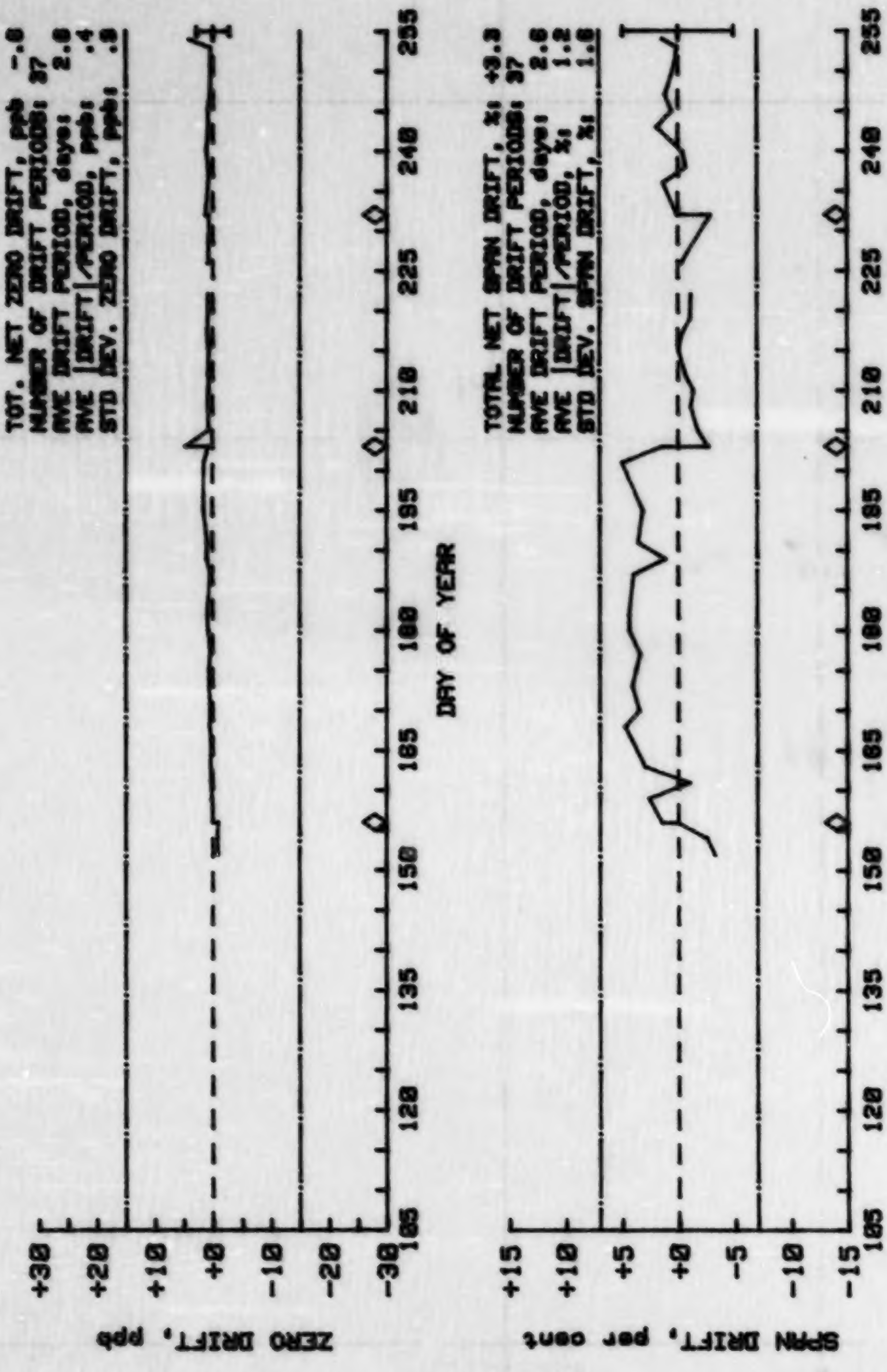


Figure 14. Zero and span drift in the Bendix 8101C (collocated) NO_2 readings during the Phase II ambient monitoring test.

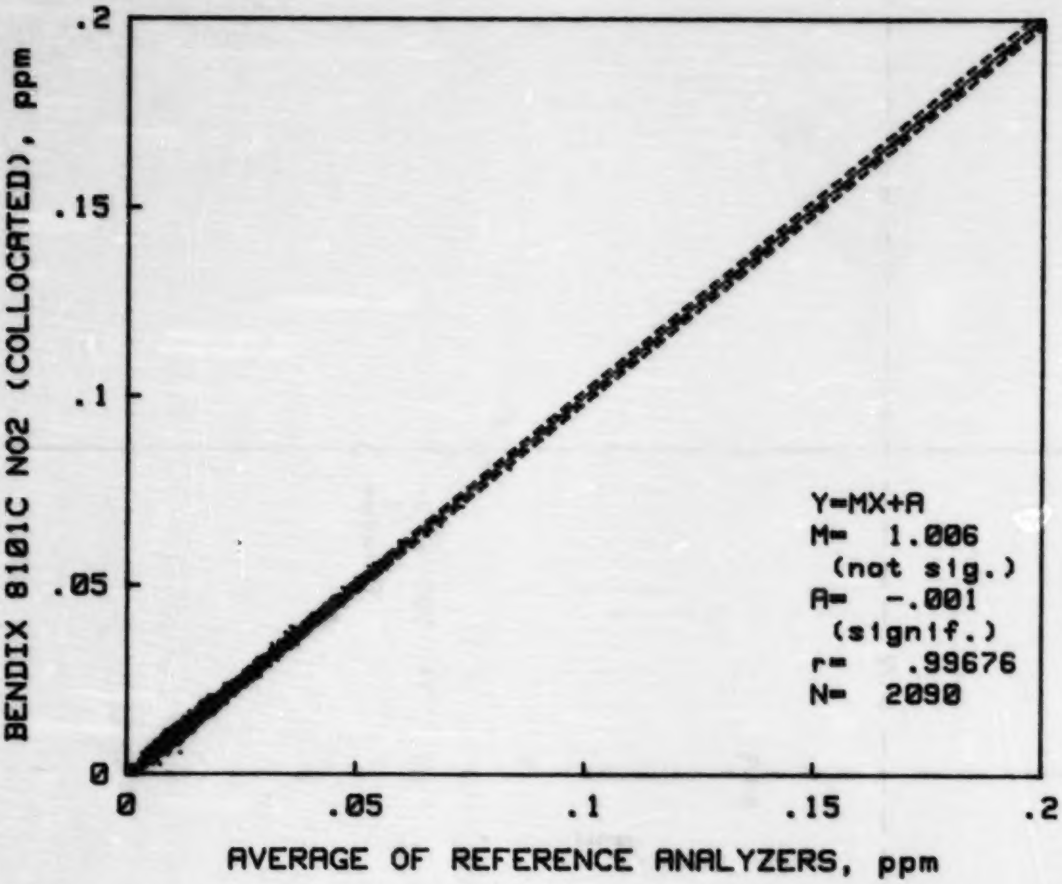
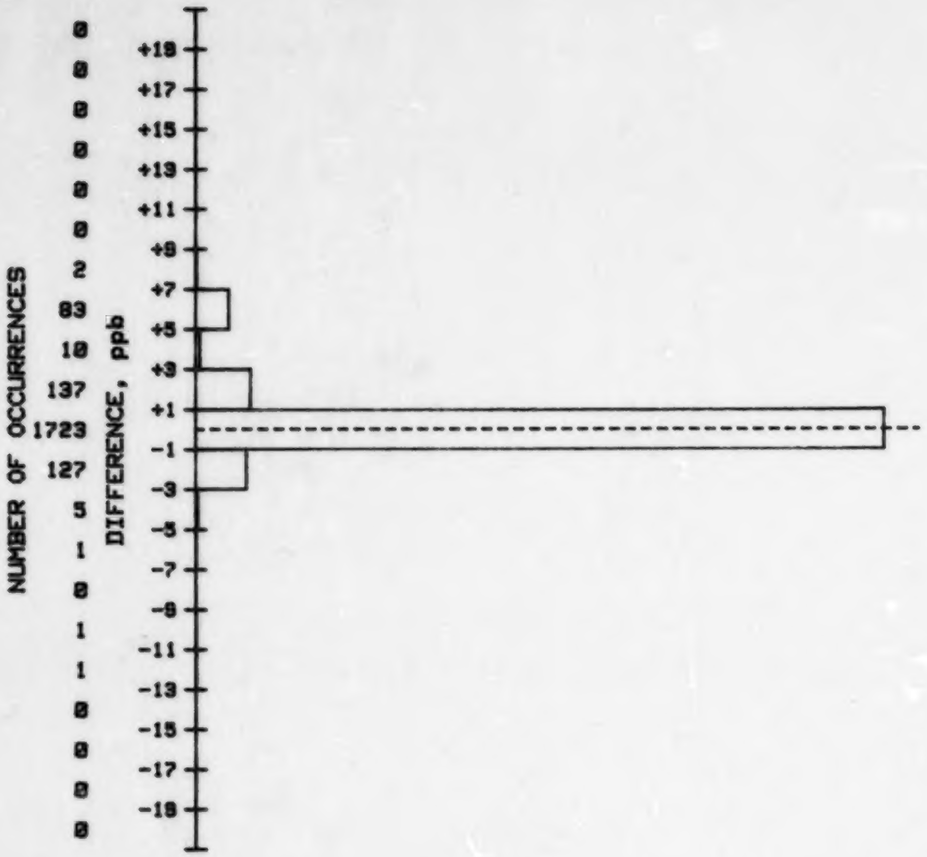


Figure 15. Correlation between the Bendix 8101C (collocated) and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BENDIX 8101C NO2 (COLLOCATED)



TOTAL No. OF DATA PAIRS:	2090
CORRELATION COEFFICIENT:	.993126
MEAN DIFFERENCE, ppb:	+.14
STD. DEVIATION OF DIFFERENCES, ppb:	1.4723
MAX. ABSOLUTE DIFFERENCE, ppb:	12
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 16. Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C (collocated) and the average of simultaneous readings from the other analyzers during Phase II test. All readings corrected for zero and span drift.

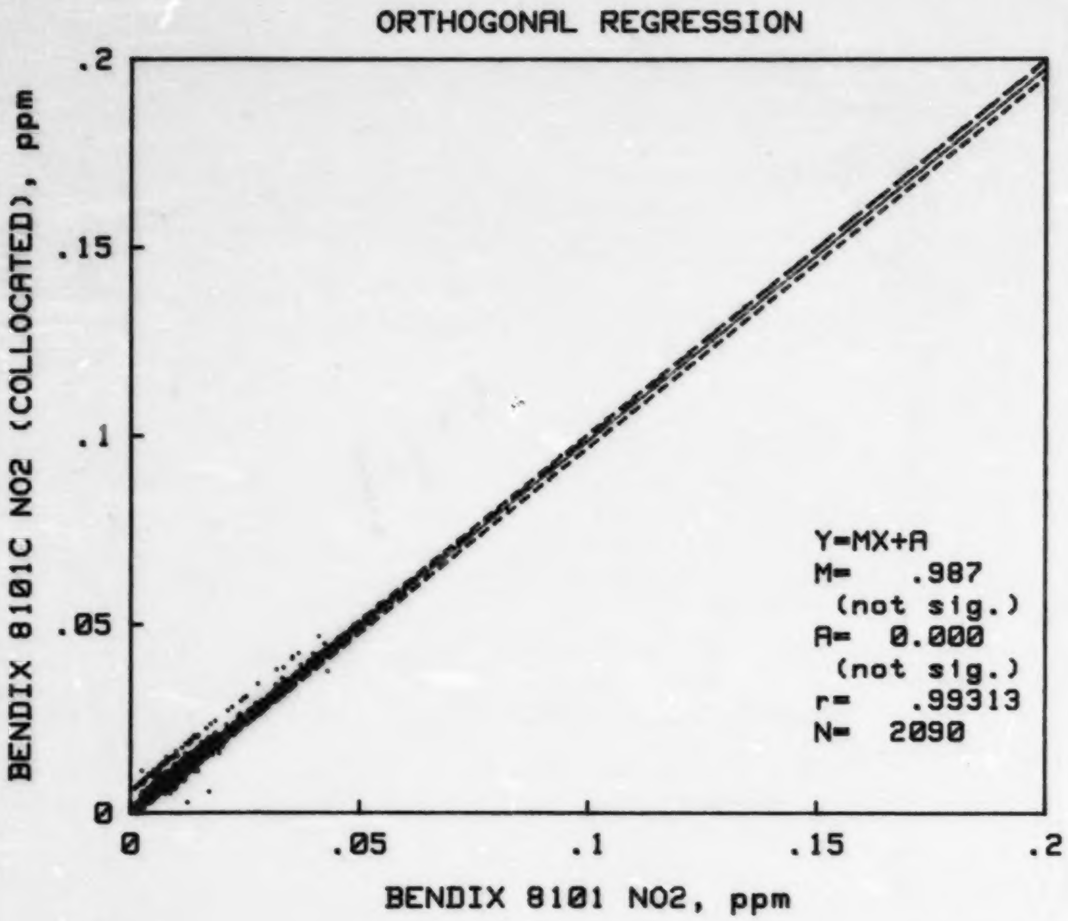
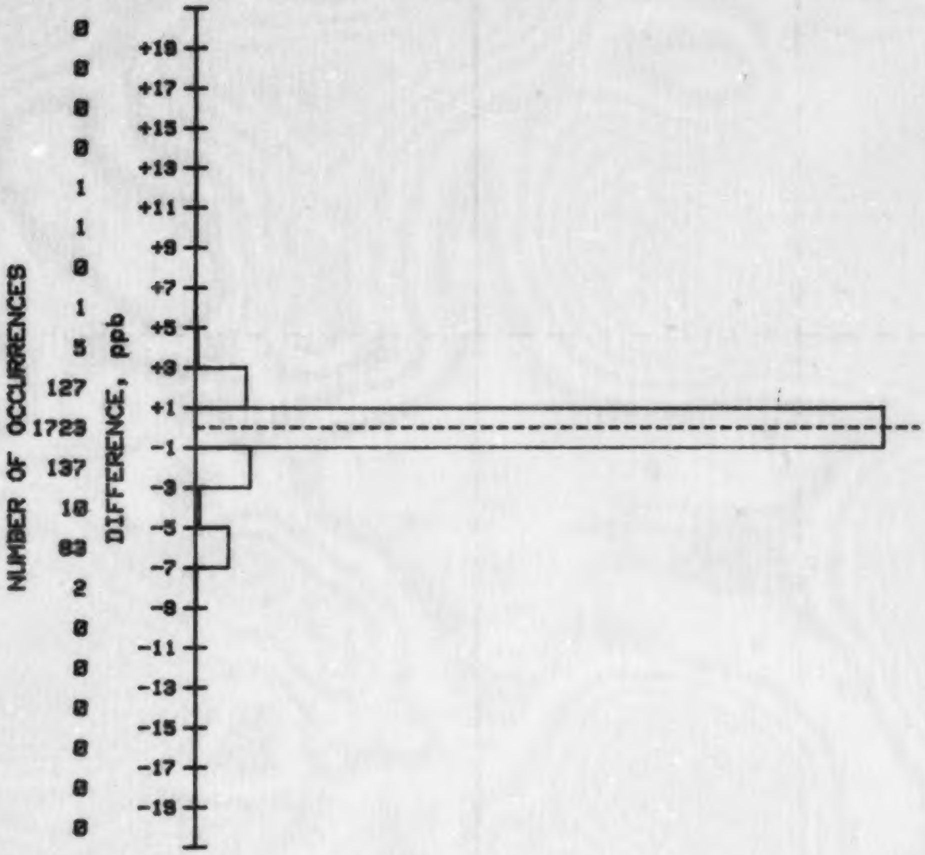


Figure 17. Correlation between the Bendix 8101C (collocated) and the Bendix 8101C (original) during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

BENDIX 8101C NO2



TOTAL No. OF DATA PAIRS:	2090
CORRELATION COEFFICIENT:	.993126
MEAN DIFFERENCE, ppb:	-.14
STD. DEVIATION OF DIFFERENCES, ppb:	1.4723
MAX. ABSOLUTE DIFFERENCE, ppb:	12
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 18. Frequency distribution of differences in hourly NO_2 ambient air readings between the Bendix 8101C (collocated) and the simultaneous readings from the Bendix 8101C (original). All readings corrected for zero and span drift.

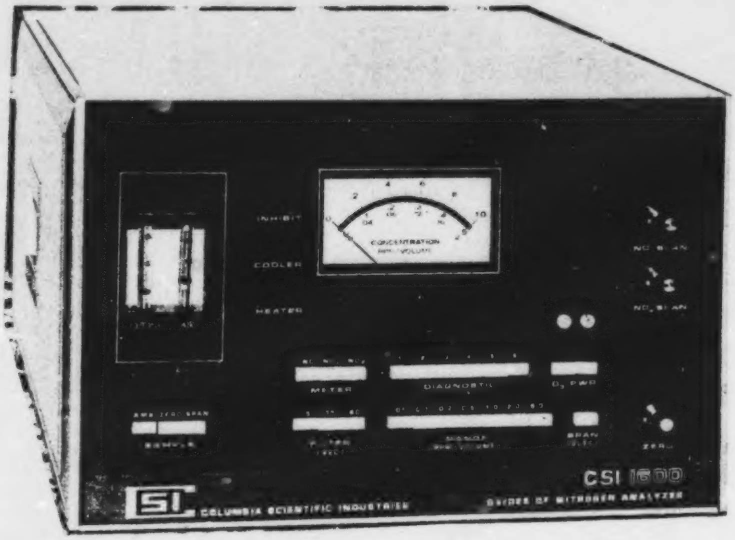

INHIBIT
COOLER
HEATER
CONCENTRATION
METER
DIAGNOSTIC
SAMPLE
SPAN
ZERO
CSI 1600
CSI COLUMBIA SCIENTIFIC INDUSTRIES
OXIDES OF NITROGEN ANALYZER

Figure 19. CSI Model 1600 Oxides of Nitrogen Analyzer (RFNA-0977-025). Columbia Scientific Industries, 11950 Jollyville Road, P.O. Box 9908, Austin, TX 78766.

General Description

The CSI (Columbia Scientific Industries) Model 1600 Oxides of Nitrogen Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with a single photomultiplier tube and reaction chamber. The input sample stream is alternately routed around the NO_2-to-NO converter and through the converter to provide measurement of NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced within the analyzer by a high voltage discharge generator. A single front panel zero control is provided that affects the zero setting of both the NO channel and the NO_x channel. Individual front panel span controls are provided for the NO channel and the NO_x channel.

To be used as a reference analyzer, the Model 1600 must be operated on the 0 to 0.5 ppm range with a Teflon® sample filter installed in the sample inlet line. It may be operated with or without any of the following options:

- Rack mounting kit
- Chassis slide kit
- Tilt stand
- Local/remote ambient, zero, span kit
- External pump unit
- Diagnostic output.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 6. CSI 1600 Laboratory Performance Test Results

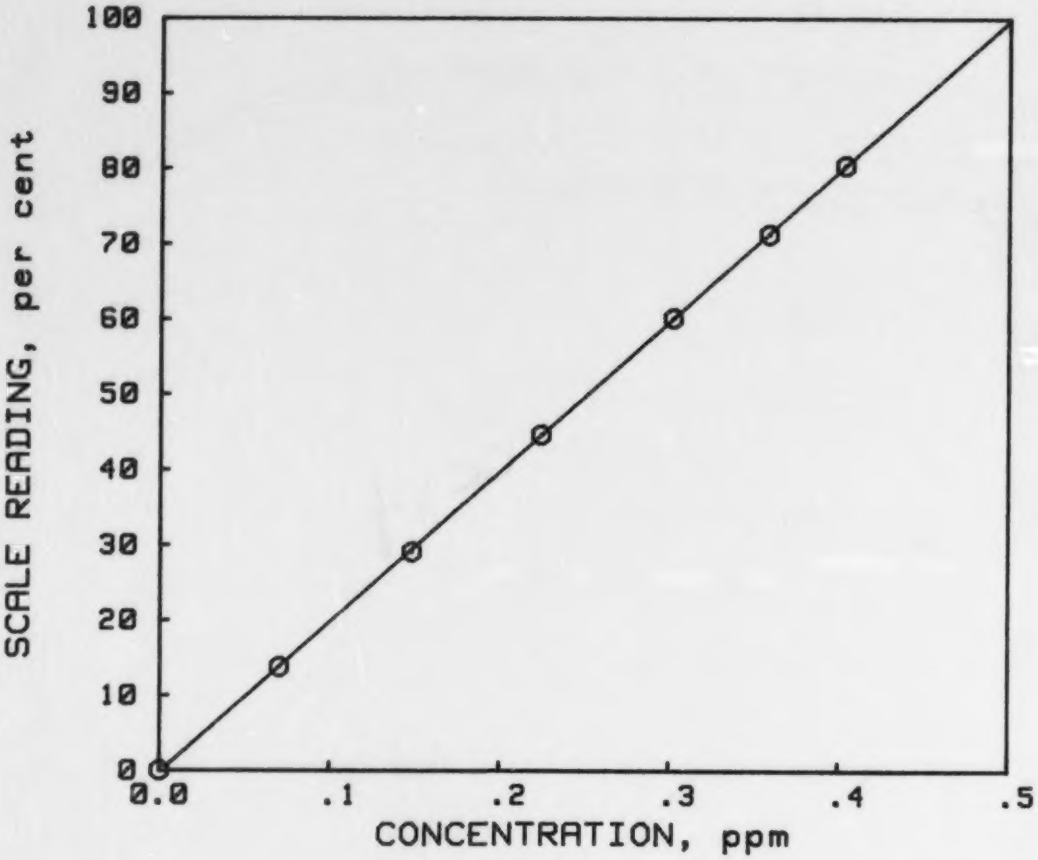
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.001
Noise – 80% URL	ppm	0.005	0.002	0.002
Lower detectable limit	ppm	0.01	0.010	0.010
Interferents	ppm			
SO_2		±0.02	0.000	0.001
NO		±0.02	<-0.001	<0.001
NH_3		±0.02	0.012	<0.001
H_2O		±0.02	<0.001	-0.004
Total interferents		≤0.04	0.013	0.006
Zero drift – 12 h	ppm	±0.02	0.002	0.004
Zero drift – 24 h	ppm	±0.02	0.001[d]	<0.001[d]
Span drift – 20% URL	%	±20.0	2.11[d]	1.41[d]
Span drift – 80% URL	%	±5.0	1.20[d]	1.87[d]
Lag time	min	20	0.1	0.4
Rise time	min	15	0.9	0.9
Fall time	min	15	0.9	0.9
Precision – 20% URL	ppm	0.020	0.001	<0.001
Precision – 80% URL	ppm	0.030	0.001	0.011

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 8850.

[d] Average of absolute values.



```
ANALYZER:     CSI                 Y = MX + A        DATA:  __X__      __Y__
MODEL:        1600
SERIAL No.:   8853                M =   199.940       1    0.000      -.039
POLLUTANT:    NO2                  95% C.I.= ± 1.258  2     .070     13.791
RANGE:          .5 ppm                                3     .148     29.143
LOCATION:     DAMDF               A =     -.219       4     .224     44.690
DATE:         06/05/81             95% C.I.= ±  .322  5     .302     60.230
DATE CODE:     81.156                                 6     .358     71.330
NAME:         RTI                 r =    .99999       7     .403     80.490
```

Figure 20. Typical calibration curve for the CSI 1600 NO_2 response.

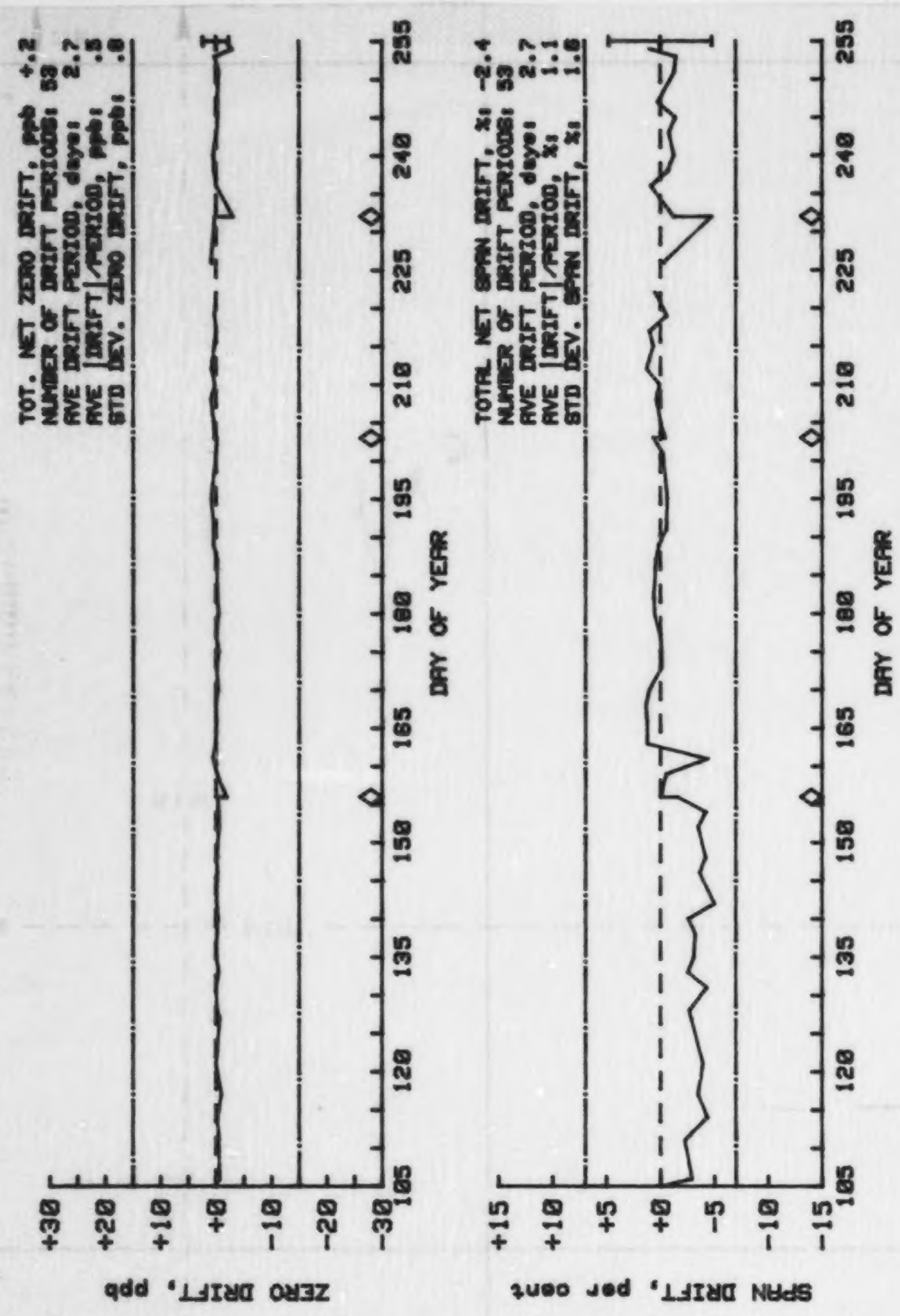


Figure 21. Zero and span drift in the CSI 1600 NO_2 readings during the Phase II ambient monitoring test.

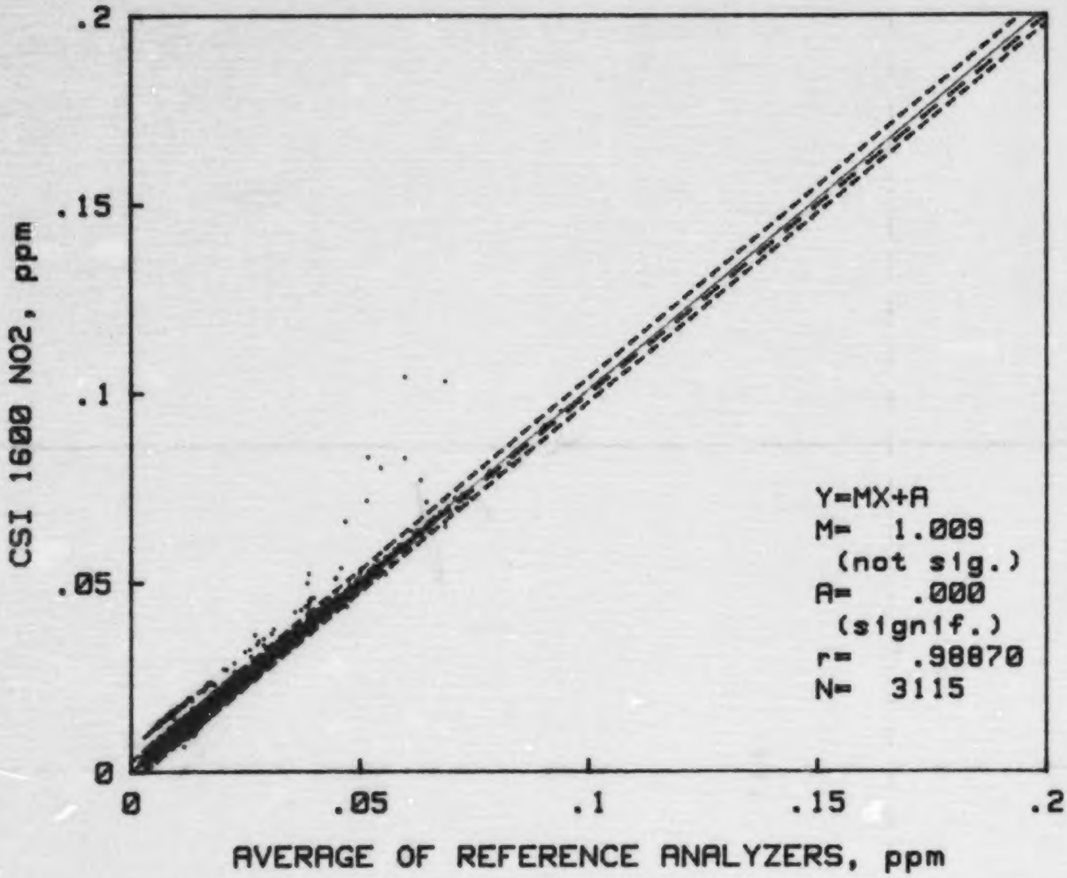
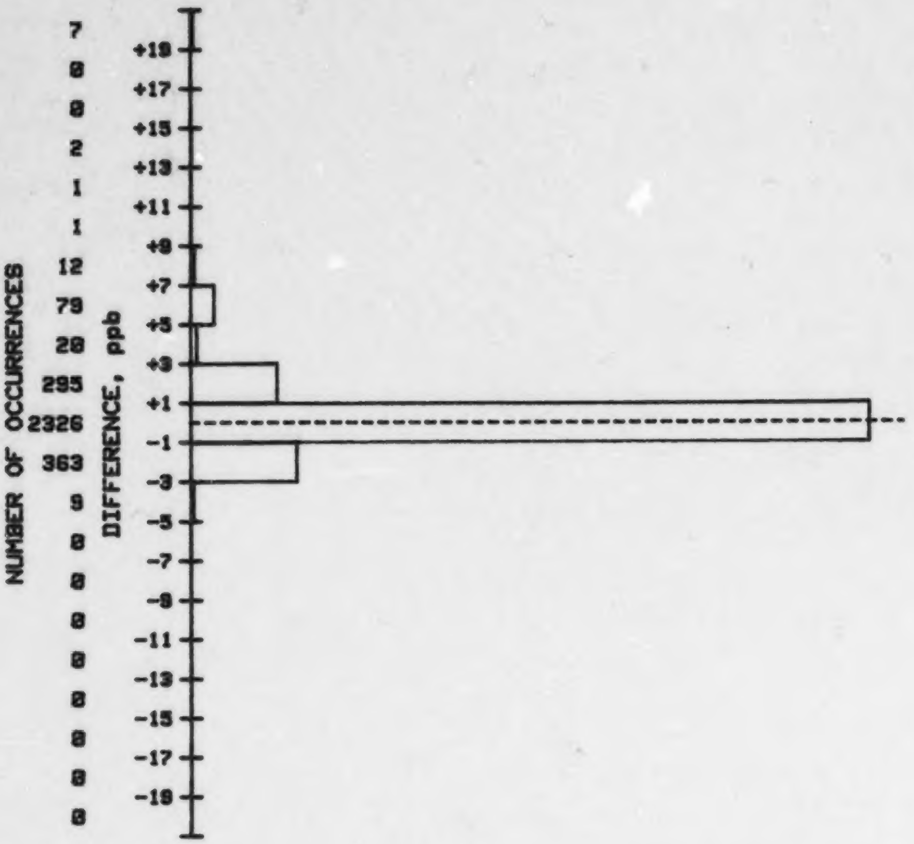


Figure 22. Correlation between the CSI 1600 and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

CSI 1600 NO2

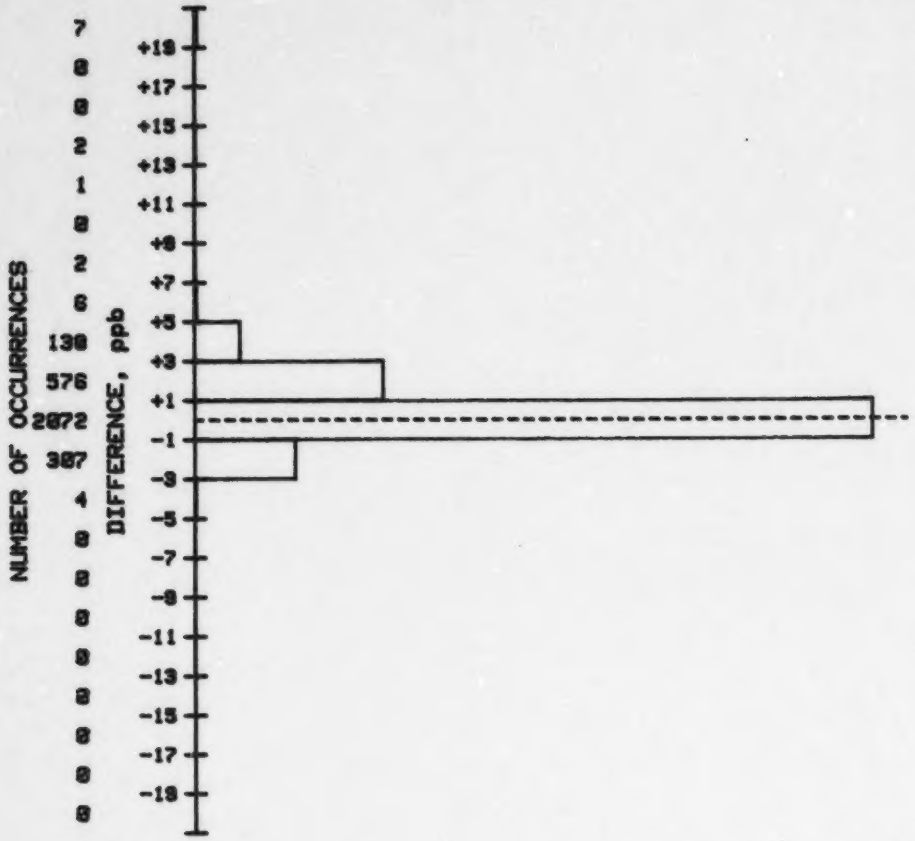


TOTAL No. OF DATA PAIRS:	3115
CORRELATION COEFFICIENT:	.988698
MEAN DIFFERENCE, ppb:	+.25
STD. DEVIATION OF DIFFERENCES, ppb:	2.0534
MAX. ABSOLUTE DIFFERENCE, ppb:	45
NO. ABSOLUTE DIFFERENCES >20:	5

Figure 23. Frequency distribution of differences in hourly NO_2 ambient air readings between the CSI 1600 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

CSI 1600 NO2



TOTAL No. OF DATA PAIRS: 3115
CORRELATION COEFFICIENT: .990557
MEAN DIFFERENCE, ppb: +.46
STD. DEVIATION OF DIFFERENCES, ppb: 1.9037
MAX. ABSOLUTE DIFFERENCE, ppb: 45
NO. ABSOLUTE DIFFERENCES >20: 5

Figure 24. Frequency distribution of differences in hourly NO_2 ambient air readings between the CSI 1600 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace Teflon® sample inlet filter	Monthly
Replace capillary sintered stainless steel filter	Yearly
Replace ozone-air reserve drier desiccant and pads	Quarterly
Replace ozone-air main drier desiccant	Monthly or before exhaustion
Replace exhaust gas scrubber charcoal and pads	Every 60 to 90 days
Replace exhaust gas scrubber unit	Annually
Lubricate rear panel squirrel cage fan	Semiannually
Clean analyzer interior and fans	Semiannually
Replace converter material	Annually or as required

Malfunctions

In August 1979, 1 month after the new analyzer had been activated initially, the PMT cooler failed. Subsequent investigation showed the problem to be physical damage, probably sustained during shipment from the factory. The manufacturer replaced the cooler under warranty.

General Comments

With the exception of the repair of the PMT cooler mentioned above, this analyzer operated throughout Phase I testing (9 months) and throughout Phase II testing (5 months) without any problems, malfunctions, or maintenance other than routine preventive maintenance.

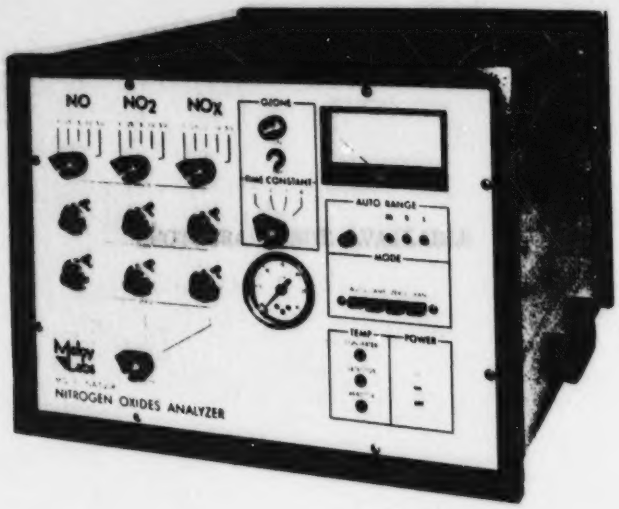


Figure 25. Meloy NA530R Nitrogen Oxides Analyzer (RFNA-1078-031). Columbia Scientific Industries, 11950 Jollyville Road, P.O. Box 9908, Austin, TX 78766.

General Description

The Meloy NA530R Nitrogen Oxides Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2, as described in Appendix A. It is equipped with dual photomultiplier tubes and dual reaction chambers. The input sample stream is split, with one-half directed to one reaction chamber, where the NO is measured, and the other half directed through the NO_2-to-NO converter to the other reaction chamber, where NO_x is measured. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced by a high voltage discharge generator. Separate zero and span controls are provided for each of the three output channels (NO, NO_2, and NO_x).

The analyzer requires an external sample pump capable of maintaining a vacuum of 200 torr at sample and ozone-air flow rates of 1,200 and 200 cm^3/min, respectively (available as an option).

When used as a reference method, the Model NA530R may be operated in any of the following configurations:

Range (ppm)	Time constant setting
0 - 0.1*	4
0 - 0.25*	3 or 4
0 - 0.5	2, 3, or 4
0 - 1.0	2, 3, or 4

The analyzer is designated for use over an extended temperature range of 10° to 40° C, inclusive (ambient temperature surrounding the analyzer), and a line voltage range of 105 to 130 Vac, inclusive. The following options are available:

- Automatic zero and span
- Vacuum gauge
- Digital panel meter
- Remote control for zero and span
- Remote zero/span control and status (pulse)
- Remote zero/span control and status (timer)
- Manual zero/span
- Vacuum pump
- Auto ranging
- Line transmitter
- Rack mount conversion (two types).

---

*Users should be aware that designation of ranges less than 0.5 ppm (500 ppb) is based on meeting the same absolute performance specifications required for the 0 to 0.5 ppm (500 ppb) range. Thus, designation of these lower ranges does not guarantee commensurably better performance than that obtained on the 0 to 0.5 ppm (500 ppb) range.

Table 7. Meloy NA530R Laboratory Performance Test Results

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.002	0.001
Noise – 80% URL	ppm	0.005	0.003	0.002
Lower detectable limit	ppm	0.01	0.009	0.010
Interferents	ppm			
SO_2		±0.02	0.003	NC
NO		±0.02	-0.005	NC
NH_3		±0.02	0.001	NC
H_2O		±0.02	0.001	NC
Total interferents		<0.04	0.011	NC
Zero drift – 12 h	ppm	±0.02	0.014	0.008
Zero drift – 24 h	ppm	±0.02	0.004[d]	0.007[d]
Span drift – 20% URL	%	±20.0	3.50[d]	NC
Span drift – 80% URL	%	±5.0	1.60[d]	NC
Lag time	min	20	<0.1	0.3
Rise time	min	15	0.6	3.9
Fall time	min	15	0.7	6.9
Precision – 20% URL	ppm	0.020	0.001	0.003
Precision – 80% URL	ppm	0.030	0.002	0.010

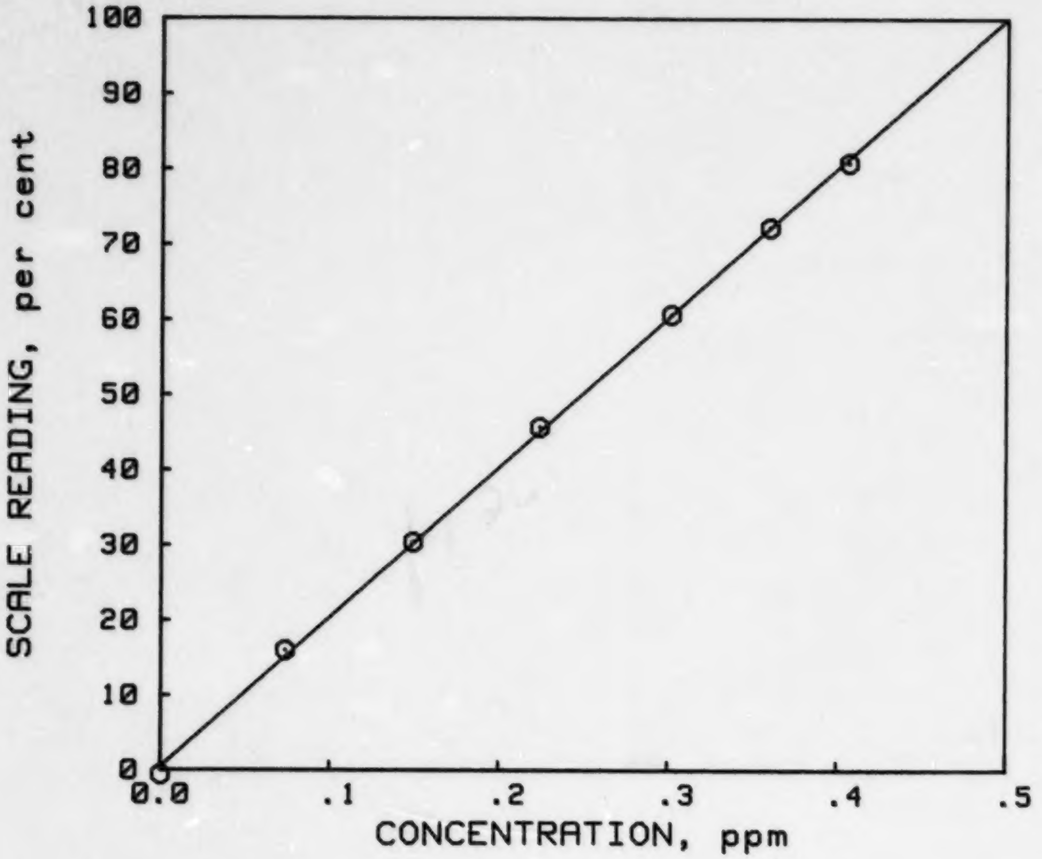
[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 8G091.

[d] Average of absolute values.

NC = Testing of this parameter was not completed.



ANALYZER: MELOY
MODEL: NA 530R
SERIAL No.: 8G091
POLLUTANT: NO2
RANGE: .5 ppm
LOCATION: DAMDF
DATE: 06/05/81
DATE CODE: 81.156
NAME: RTI

$Y = MX + A$

M = 199.336
95% C.I.= ± 5.131

A = .453
95% C.I.= ± 1.320

r = .99975

DATA:	X	Y
1	0.000	-.649
2	.074	15.965
3	.149	30.383
4	.224	45.660
5	.302	60.660
6	.360	72.220
7	.406	80.850

Figure 26. Typical calibration curve for the Meloy NA530R NO_2 response.

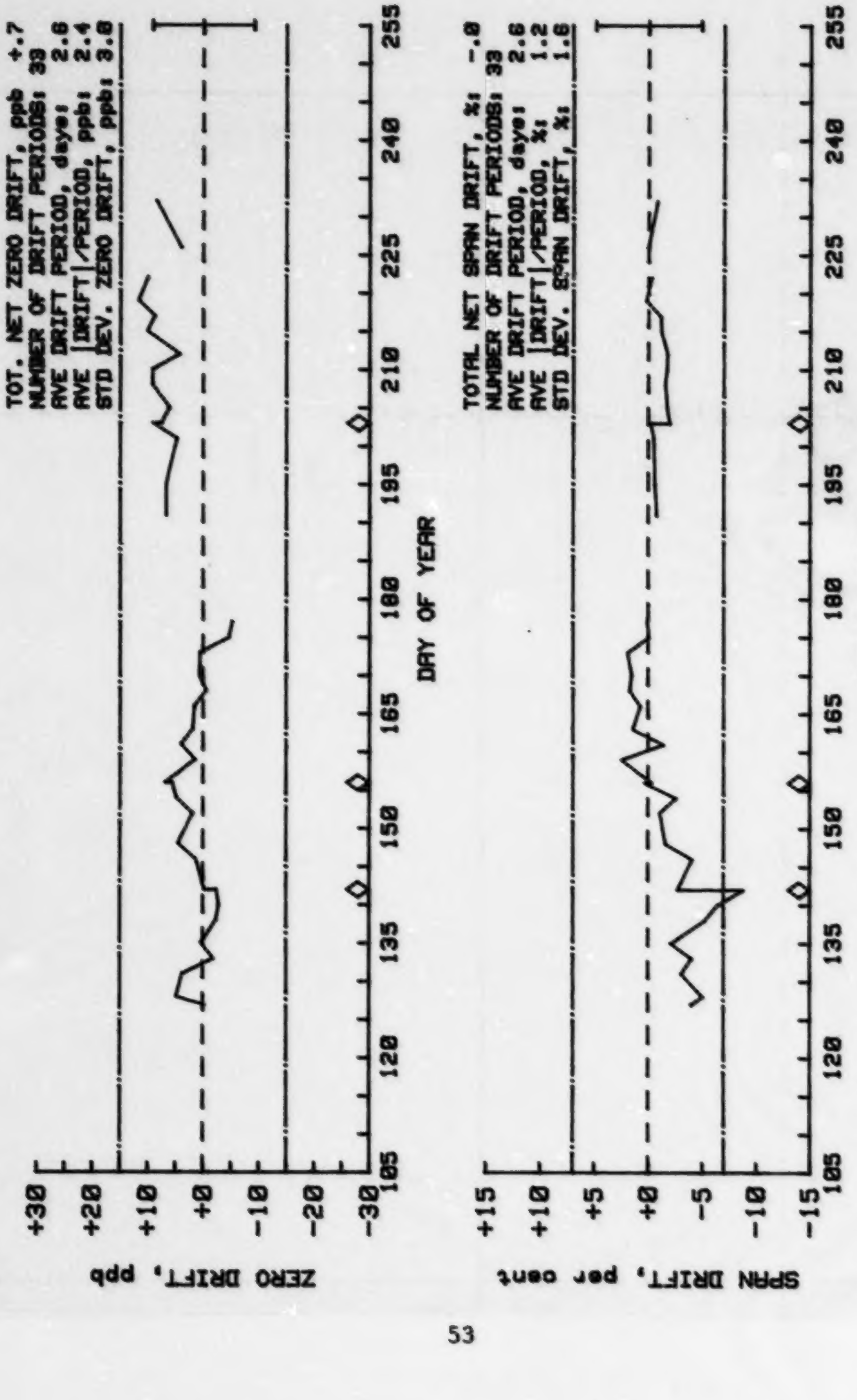


Figure 27. Zero and span drift in the Meloy NA530R NO$_2$ readings during the Phase II ambient monitoring test.

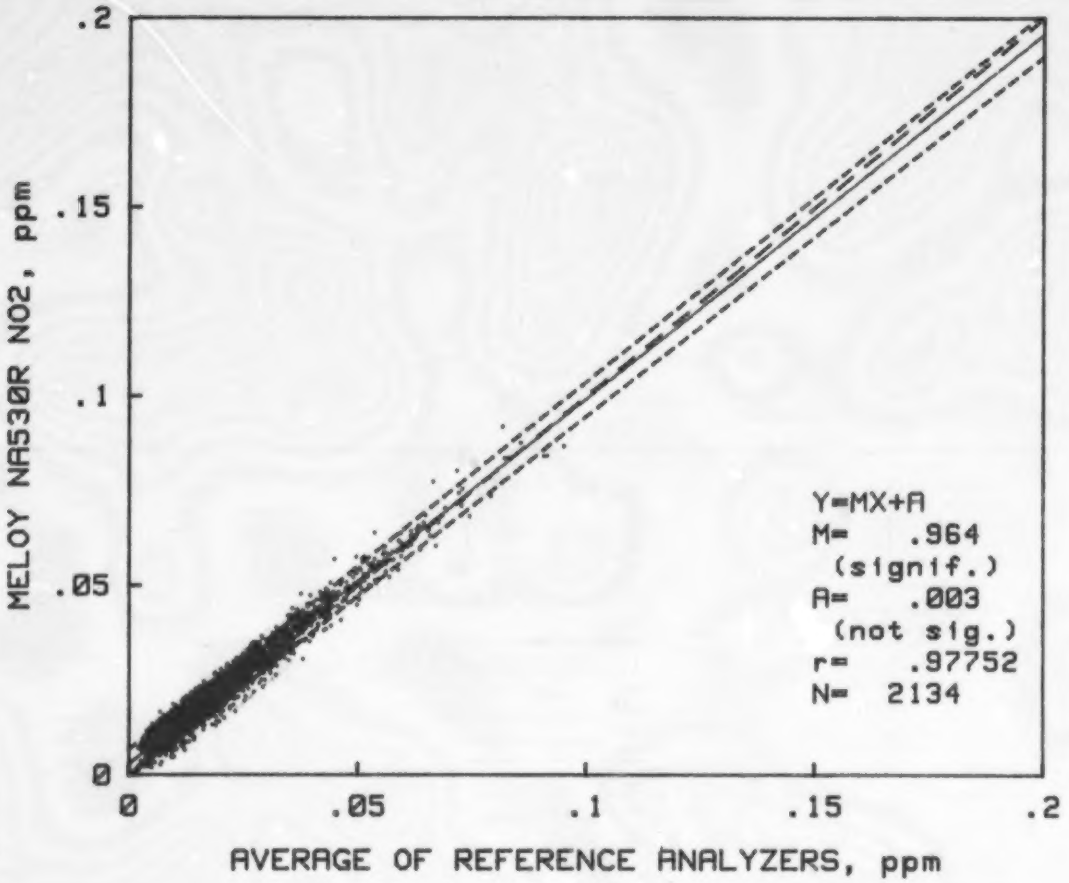
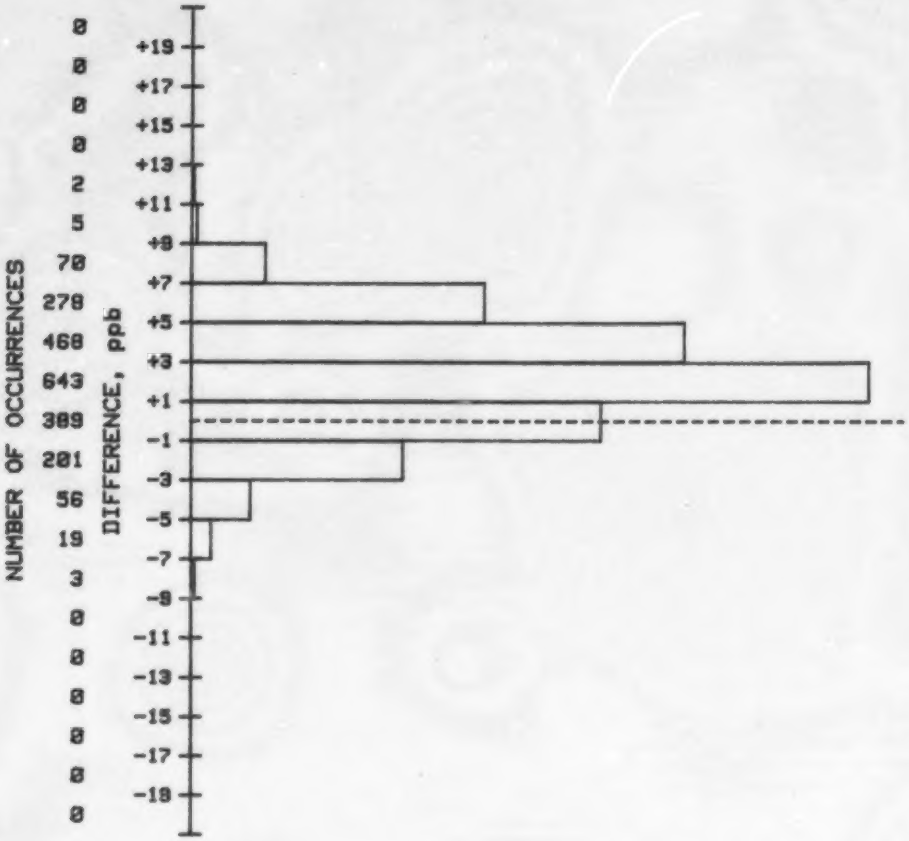


Figure 28. Correlation between the Meloy NA530R and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

MELOY NA530R NO2

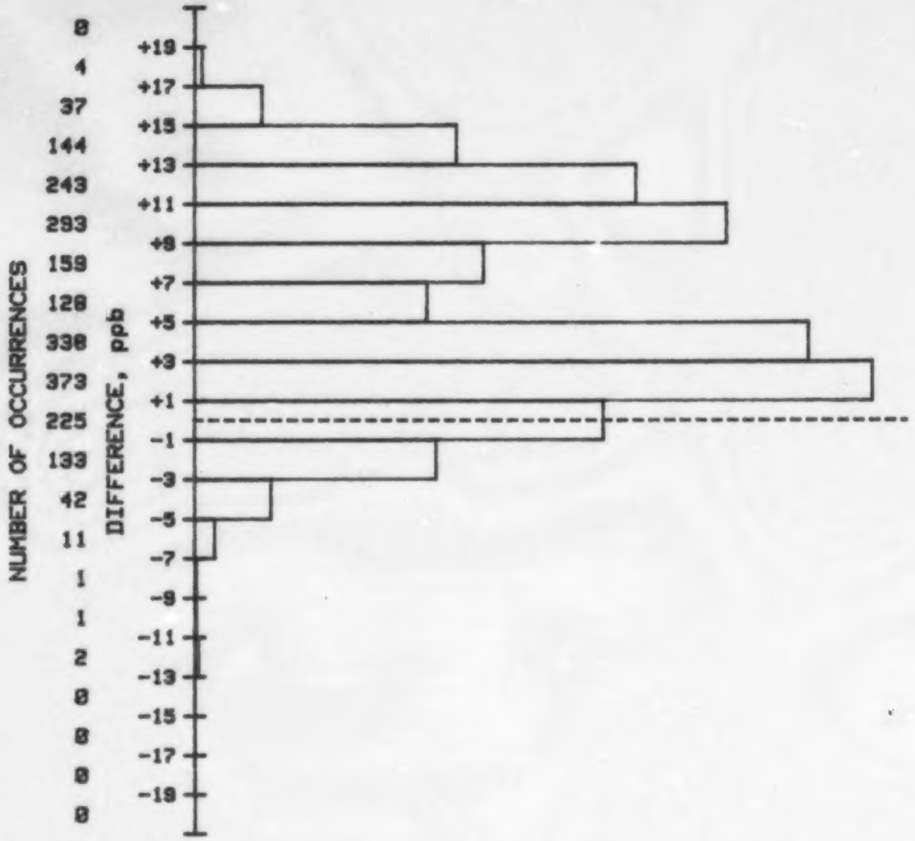


TOTAL No. OF DATA PAIRS: 2134
CORRELATION COEFFICIENT: .977522
MEAN DIFFERENCE, ppb: +2.18
STD. DEVIATION OF DIFFERENCES, ppb: 2.8218
MAX. ABSOLUTE DIFFERENCE, ppb: 12
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 29. Frequency distribution of differences in hourly NO_2 ambient air readings between the Meloy NA530R and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

MELOY NA530R NO2



TOTAL No. OF DATA PAIRS:	2134
CORRELATION COEFFICIENT:	.923357
MEAN DIFFERENCE, ppb:	+5.68
STD. DEVIATION OF DIFFERENCES, ppb:	5.1771
MAX. ABSOLUTE DIFFERENCE, ppb:	18
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 30. Frequency distribution of differences in hourly NO_2 ambient air readings between the Meloy NA530R and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Meloy readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace or clean particulate filters	3 to 6 months
Replace or clean flow control orifices and capillaries	6 to 12 months
Clean zero and span valves	6 to 12 months
Replace zero and span valves	Triannually
Replace charcoal filter	6 to 12 months or when required
Service ozone generator	Annually or when required
Replace purifier for ozone generator	6 to 12 months
Replace or service vacuum pump	Biannually
Check vacuum pressure regulator	When required
Replace NO_2-to-NO converter	Annually or when required
Replace or clean window filter of reaction chamber	Annually
Clean chassis fan air filter	Annually
Perform electronic alignment	When required

Malfunctions

The time required for maintenance, adjustment, and repair of the analyzer amounted to a significant portion of the total Phase I test period. This time requirement was excessive and unusual for an analyzer of this type, thus warranting special mention. During the 15-month test period, the analyzer was offsite for factory repair three times for an estimated total of 6.2 months. An additional 1 month was required for onsite repair and adjustment work. An estimated total of 8 months' operation was lost due to analyzer malfunctions of all types, amounting to 53 percent of the Phase I test period.

During the Phase II test, the time required for maintenance and repair diminished somewhat, but still remained above average. The time spent on repairs and maintenance of each of the analyzers during this test ranged from 0 to 96 days and averaged 28.4 days per analyzer. The Meloy NA530R analyzer required 49 of the 150 days in the test for corrective maintenance.

General Comments

Phase I testing of this analyzer was attempted several times between July 1979 and December 1980. Because of repeated test failures by this analyzer, numerous component malfunctions, and various other test difficulties not related directly to this analyzer, some Phase I tests were never successfully completed. In January 1981 (after 15 months of testing attempts), EPA project personnel suspended the testing, postponing completion of the test indefinitely because of overall postdesignation testing project time and budgetary constraints.

This analyzer is equipped with separate zero/span controls for the NO, NO_2, and NO_x channels. These controls, however, cannot be used to effect a balance between the response of the NO and NO_x channels on an NO atmosphere. Balance is achieved during the adjustment of the balance and gain circuitry of the Lock-In Amplifier (see Section VI, Maintenance, Subsection E.1.c.2, of the operating manual). Although the manual states that these adjustments need not be performed routinely, experience during these tests indicated that the balance is subject to frequent drift requiring frequent adjustment. In August 1981, just prior to the end of Phase II testing, adjustments to the balance were necessary six times within 1 month.

In March 1980 during Phase I testing, the analyzer failed three of four 80-percent-of-scale span drift tests (Days 2, 3, and 4), with drift values of -6.5, +15.7, and -11.8 percent. The fourth test was passed with a drift value of +4.4 percent. One of four 20-percent-of-scale drift tests was also failed (Day 4) at a value of -28.5 percent. The drift performance seemed to be more influenced by changes in line voltage to the analyzer than by changes in the temperature of the air surrounding the analyzer. However, changes in either parameter seemed to affect performance.

Upon examination of the strip chart recordings produced by the analyzer during the tests, it was noted that a consistent shift of 2 to 2½ percent of chart occurred between members of pairs of P_7-P_{12} test points. The latter member of a point pair (i.e., the even test points) consistently came to equilibrium 2 to 2½ percent of chart above the previous point. Although each of the P_7-P_{12} points appeared to have come to equilibrium before the next point was generated, it was postulated that the odd/even point pair behavior could be attributable to long, unresolved equilibrium times. Such a problem may or may not have contributed to the drift test failures.

On March 21, 1980, additional, modified rise time tests were conducted to investigate the possibility of unresolved equilibrium times. During these tests, the analyzer was transferred from a zero air matrix to an 80-percent-of-scale span matrix and allowed to sample that matrix for 3½ hours. The rise time to 95 percent of the final response required 40 minutes; rise time to 100 percent required 90 minutes. During the test, several apparent equilibrium points were reached and held for as much as 20 minutes before the response resumed movement. The successful response time tests recorded during the March 11 through 18 tests are now believed to be in error because of the selection of a false equilibrium point as the final equilibrium point for the analyzer's responses to P_9 and L_2 points. Subsequent work by manufacturer representatives onsite demonstrated that this problem was caused by overly conservative settings of the analyzer's noise suppression circuitry.

MONITOR LABS 8440E

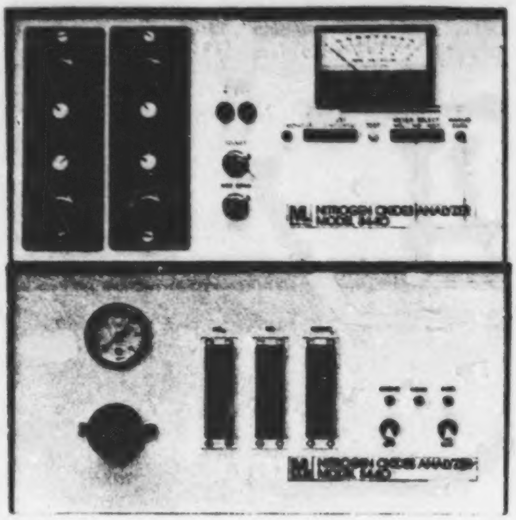

ML NITROGEN OXIDES ANALYZER MODEL 8440
ML NITROGEN OXIDES ANALYZER MODEL 8440

Figure 31. Monitor Labs Model 8440E Nitrogen Oxides Analyzer (RFNA-0677-021). Monitor Labs, Inc., 10180 Scripps Ranch Boulevard, San Diego, CA 92131.

General Description

The Monitor Labs Model 8440E Nitrogen Oxides Analyzer is no longer in production, having been replaced by the Model 8840. The reference designation for the analyzer is still in effect, however.

The analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with dual photomultiplier tubes and dual reaction chambers. The input sample stream is split, with one-half directed to one reaction chamber, where the NO is measured, and the other half directed through the NO_2-to-NO converter to the other reaction chamber, where NO_x is measured. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced by a high voltage discharge generator. Separate front panel zero and span controls are provided for both the NO channel and the NO_x channel. Trim potentiometers for the NO_2 channel are provided on the Difference Amplifier PCB inside the instrument.

To be used as a reference analyzer, the Model 8440E must be operated on the 0 to 0.5 ppm range (position 2 of the range switch), with a time constant setting of 20 seconds, and with or without any of the following options:

- Sample particulate matter filter with TFE filter element
- Zero/span valves
- Flowmeters
- Status outputs
- Rack mount
- Ozone dry air or ozone dry air/no Drierite.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 8. Monitor Labs 8440E Laboratory Performance Test Results

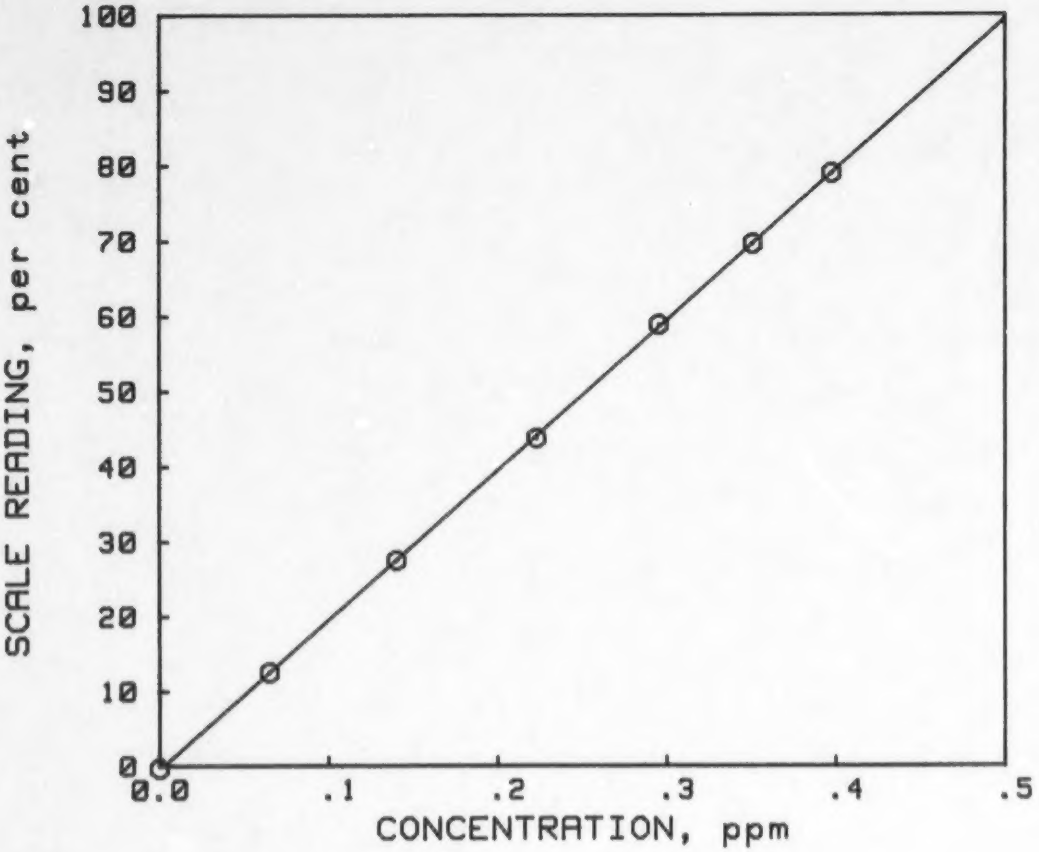
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.001
Noise – 80% URL	ppm	0.005	0.002	0.004
Lower detectable limit	ppm	0.01	0.010	0.010
Interferents	ppm			
SO_2		±0.02	<0.001	<0.001
NO		±0.02	0.001	0.018
NH_3		±0.02	<-0.001	<0.001
H_2O		±0.02	-0.001	-0.003
Total interferents		<0.04	0.005	0.022
Zero drift – 12 h	ppm	±0.02	0.002	0.003
Zero drift – 24 h	ppm	±0.02	0.001[d]	0.002[d]
Span drift – 20% URL	%	±20.0	4.58[d]	3.07[d]
Span drift – 80% URL	%	±5.0	3.42[d]	2.59[d]
Lag time	min	20	<1.0	<1.0
Rise time	min	15	1.2	1.8
Fall time	min	15	0.9	1.4
Precision – 20% URL	ppm	0.020	0.002	<0.001
Precision – 80% URL	ppm	0.030	0.002	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 125.

[d] Average of absolute values.



```
ANALYZER:    MONITOR LABS   Y = MX + A       DATA:  __X__     __Y__
MODEL:       8440E
SERIAL No.:  125            M =   199.802       1   0.000      -.390
POLLUTANT:   NO2             95% C.I.= ± 1.600  2    .065     12.488
RANGE:        .5 ppm                            3    .140     27.463
LOCATION:    DAMDF          A =     -.494       4    .223     43.720
DATE:        07/22/81        95% C.I.= ±  .402  5    .295     58.880
DATE CODE:    81.203                            6    .351     69.600
NAME:        RTI            r =    .99938       7    .398     78.930
```

Figure 32. Typical calibration curve for the Monitor Labs 8440E NO_2 response.

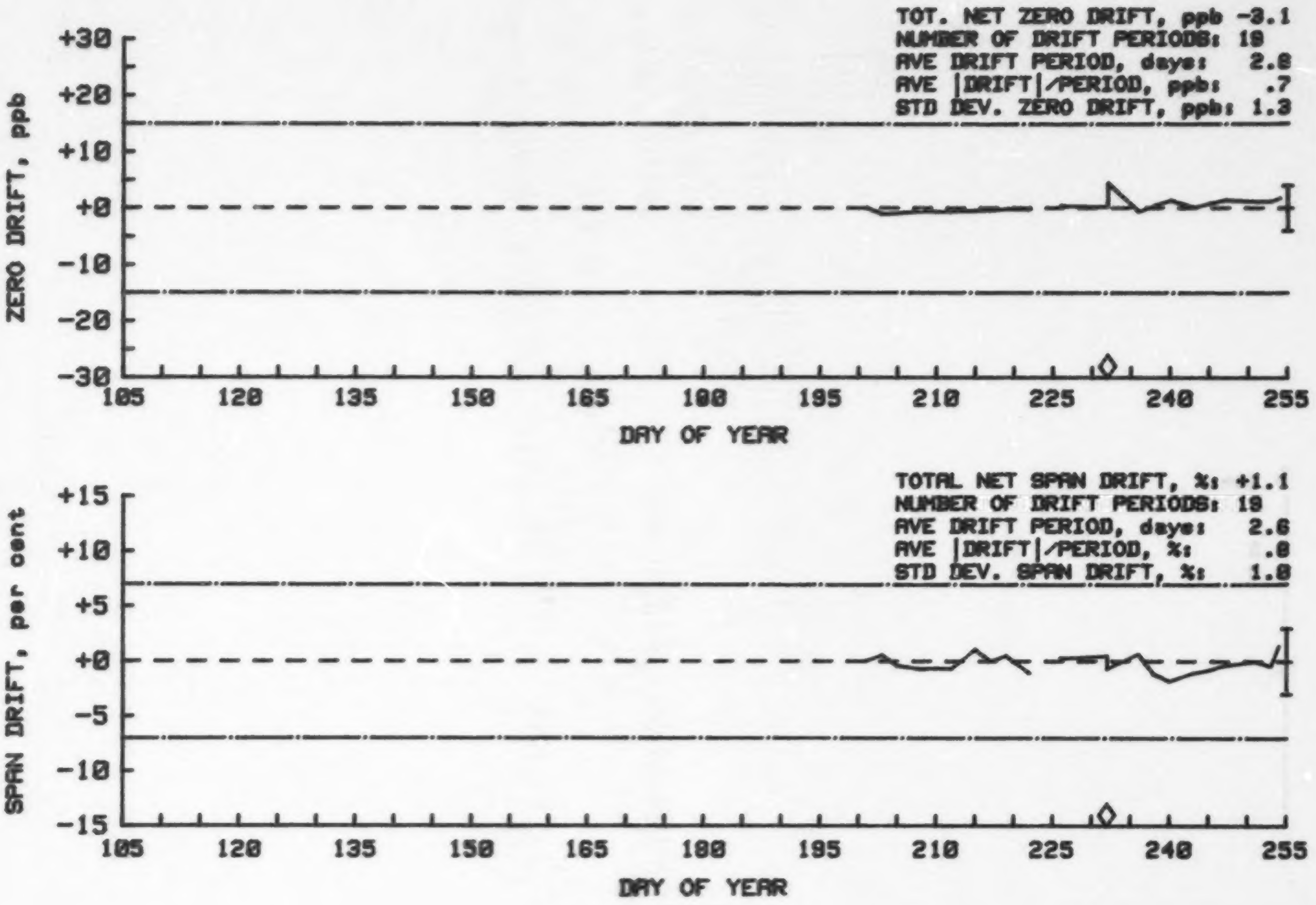


Figure 33. Zero and span drift in the Monitor Labs 8440E NO_2 readings during the Phase II ambient monitoring test.

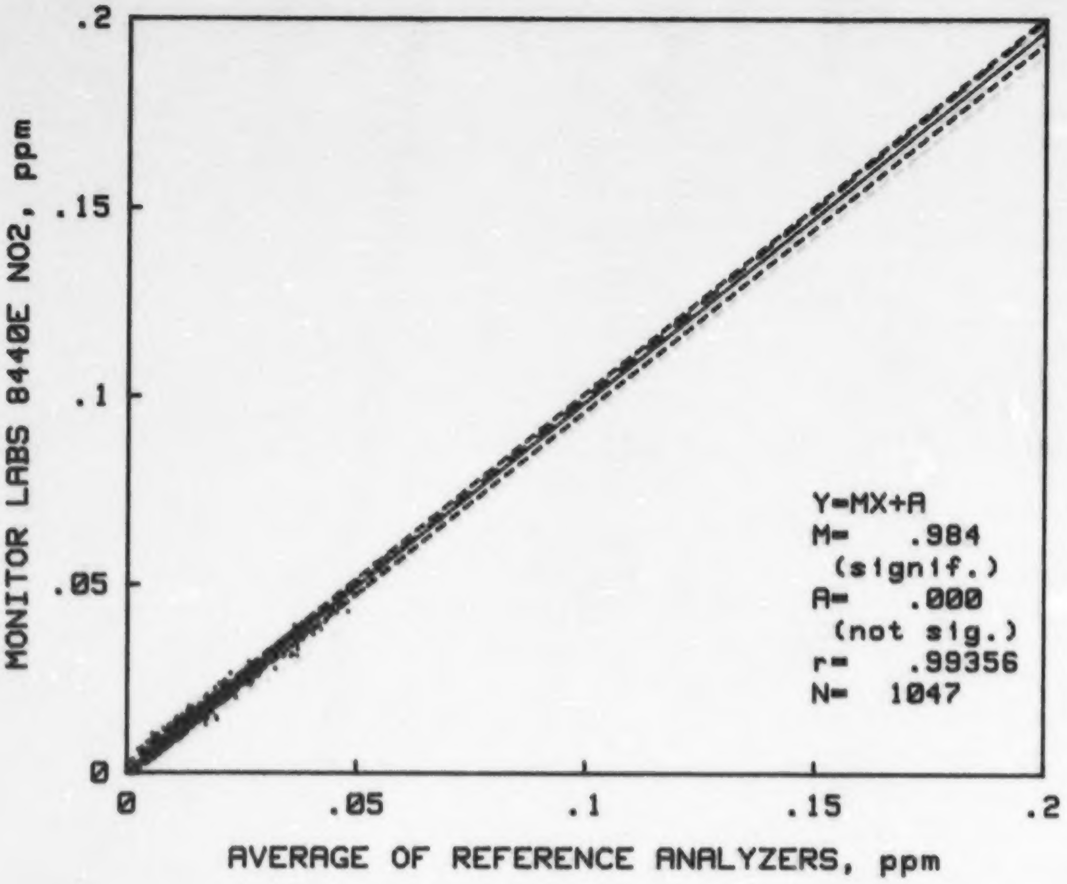
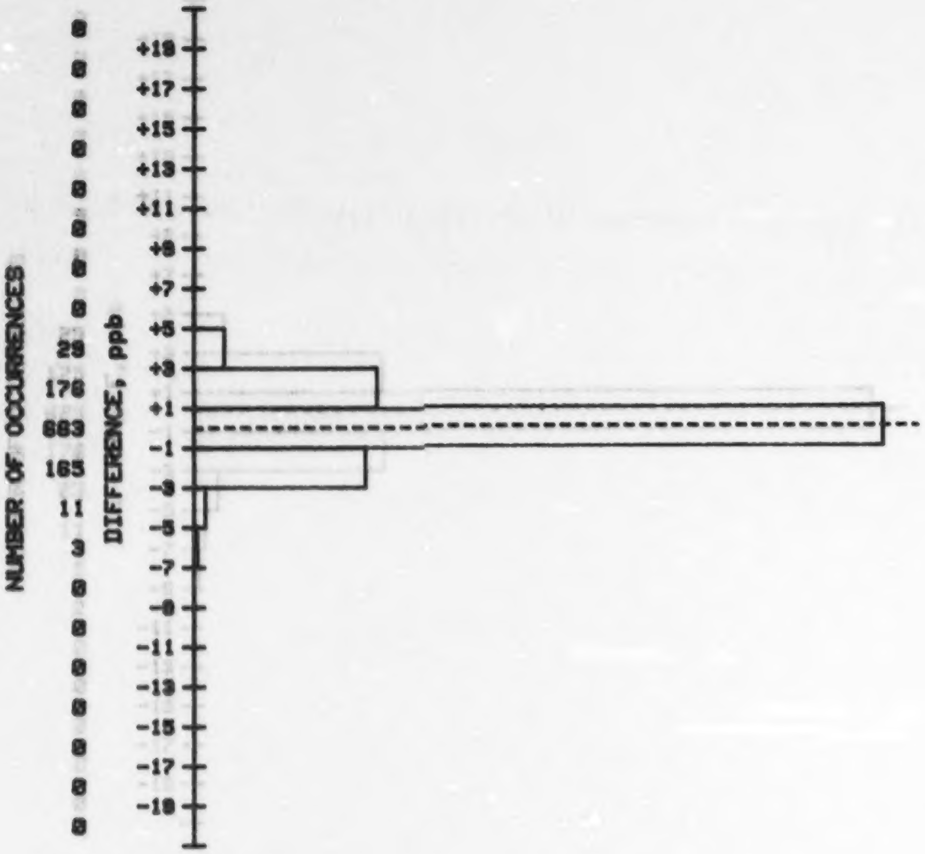


Figure 34. Correlation between the Monitor Labs 8440E and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

MONITOR LABS 8440E NO2

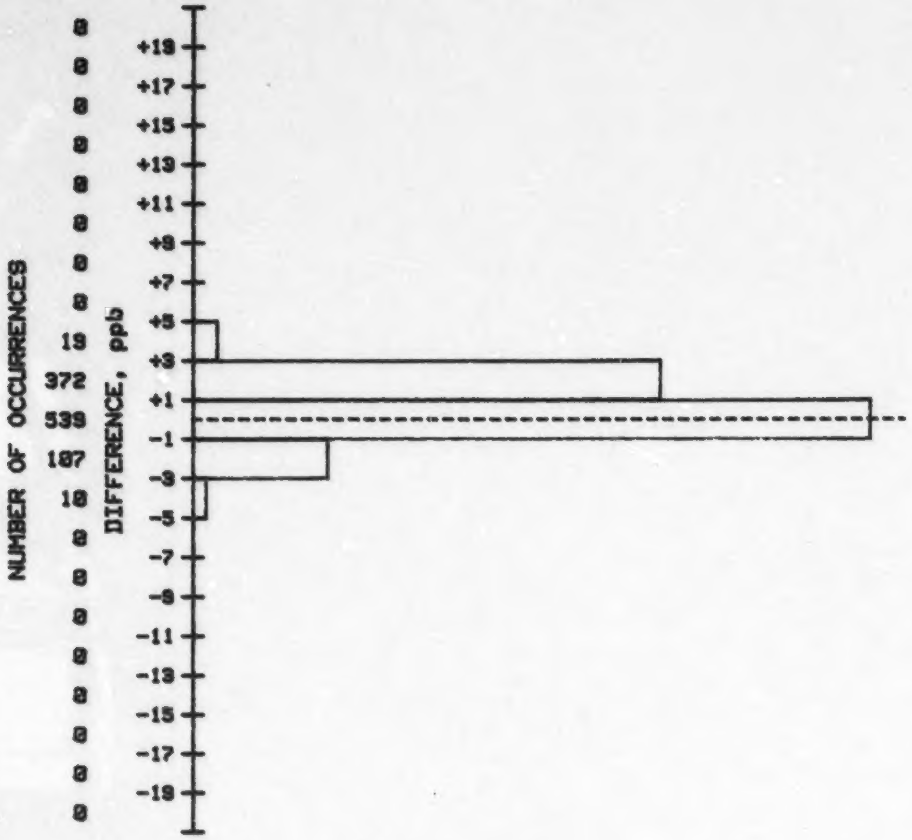


TOTAL No. OF DATA PAIRS: 1047
CORRELATION COEFFICIENT: .993564
MEAN DIFFERENCE, ppb: +.13
STD. DEVIATION OF DIFFERENCES, ppb: 1.2967
MAX. ABSOLUTE DIFFERENCE, ppb: 6
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 35. Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

MONITOR LABS 8440E NO2



TOTAL No. OF DATA PAIRS:	1047
CORRELATION COEFFICIENT:	.993257
MEAN DIFFERENCE, ppb:	+.52
STD. DEVIATION OF DIFFERENCES, ppb:	1.3298
MAX. ABSOLUTE DIFFERENCE, ppb:	5
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 36. Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Monitor Labs readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace chassis fan	When required
Replace chopper bearings	When required
Replace chopper motor	When required
Replace chopper drive belt	Every 1 to 6 months or when required
Clean isoflow module	When required
Replace sample particulate filter	Monthly
Clean or replace flowmeters	When required
Clean pneumatic lines and filters	When required
Clean reaction chambers	When required
Service vacuum pump	When required
Clean or replace fan filter	Every 15 to 30 days
Replace ozone generator	When required
Replace ozone scrubber	Every 3 months or when required
Replace ozone air drier column	Weekly
Replace NO_2-to-NO converter	When required

Malfunctions

This analyzer was refurbished by Monitor Labs just prior to Phase I testing. When it was activated for the Phase I test on May 15, 1980, it had not been run since being returned from the factory. On June 12, after only 1 month of operation, noise in the output signal was traced to a NO_x reaction chamber that was severely contaminated with nitric acid. Such contamination is usually indicative of operation without an air dryer on the ozone-air inlet. However, the analyzer had been operated with the proper dryer in place at all times since its activation in May. The analyzer was returned to the factory where the damage was repaired under warranty. No further problems were encountered during the Phase I testing.

In December 1980, after Phase I testing was complete, the response of the NO channel to NO span atmospheres began to degrade until it was at a level of 30 to 40 percent of nominal. Subsequent investigation showed the problem to be a failure in the NO channel PMT circuitry. After several attempts at both onsite and factory troubleshooting and repair, the entire PMT/reactor chamber housing was replaced in July 1981. Thereafter, Phase II testing was conducted normally. However, 96 days of operation out of the 150-day Phase II test were lost before this malfunction was resolved.

General Comments

Prior to Phase II testing, this analyzer was converted to the use of a Monitor Labs prepackaged, disposable charcoal scrubber unit on the recommendation of a Monitor Labs service representative. Prior to the conversion, the scrubber unit had been user-refillable.

Figure 37. Monitor Labs Model 8840 Nitrogen Oxides Analyzer (RFNA-0280-042). Monitor Labs, Inc., 10180 Scripps Ranch Boulevard, San Diego, CA 92131.

General Description

The Monitor Labs Model 8840 Nitrogen Oxides Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with dual photomultiplier tubes and dual reaction chambers. The input sample stream is split, with one-half directed to one reaction chamber where the measurement of NO is accomplished and the other half directed through the NO_2-to-NO converter to the other reaction chamber where NO_x is measured. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced by a high voltage discharge generator. Separate front panel zero and span controls are provided for both the NO channel and the NO_x channel.

To be used as a reference analyzer, the Model 8840 may be operated on a range of either 0 to 0.5 ppm or 0 to 1.0 ppm, with an internal time constant setting of 60 seconds and a Teflon® sample filter installed in the sample inlet line. It may be operated with or without any of the following options:

- Flowmeter
- Rack ears
- Slides
- Zero/span valves
- Valve/relay
- Status
- Input power transformer, 100 Vac, 50/60 Hz
- Input power transformer, 220/240 Vac, 50 Hz
- Pump pac assembly (115 Vac)
- Pump pac assembly (100 Vac)
- Pump pac assembly (220/240 Vac)
- Rack mount panel assembly
- Pump, 115 Vac 50/60 Hz
- Pump, 100 Vac 50/60 Hz
- Pump, 220/240 Vac 50 Hz
- Recorder output, 1 V
- Recorder output, 100 mV
- Recorder output, 10 mV
- DAS output, 1 V
- DAS output, 100 mV
- DAS output, 10 mV
- Ozone dry air
- Ozone dry air/no Drierite®.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 9. Monitor Labs 8840 Laboratory Performance Test Results

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	0.001	0.001
Noise – 80% URL	ppm	0.005	0.002	0.002
Lower detectable limit	ppm	0.01	0.011	0.009
Interferents	ppm			
SO_2		±0.02	e	0.000
NO		±0.02	e	-0.005
NH_3		±0.02	e	0.000
H_2O		±0.02	e	-0.006
Total interferents		<0.04	e	0.012
Zero drift – 12 h	ppm	±0.02	0.004	0.005
Zero drift – 24 h	ppm	±0.02	0.002[d]	0.001[d]
Span drift – 20% URL	%	±20.0	8.15[d]	2.94[d]
Span drift – 80% URL	%	±5.0	2.71[d]	1.10[d]
Lag time	min	20	0.1	<1.0
Rise time	min	15	3.0	2.5
Fall time	min	15	3.0	2.6
Precision – 20% URL	ppm	0.020	0.001	0.001
Precision – 80% URL	ppm	0.030	0.001	0.002

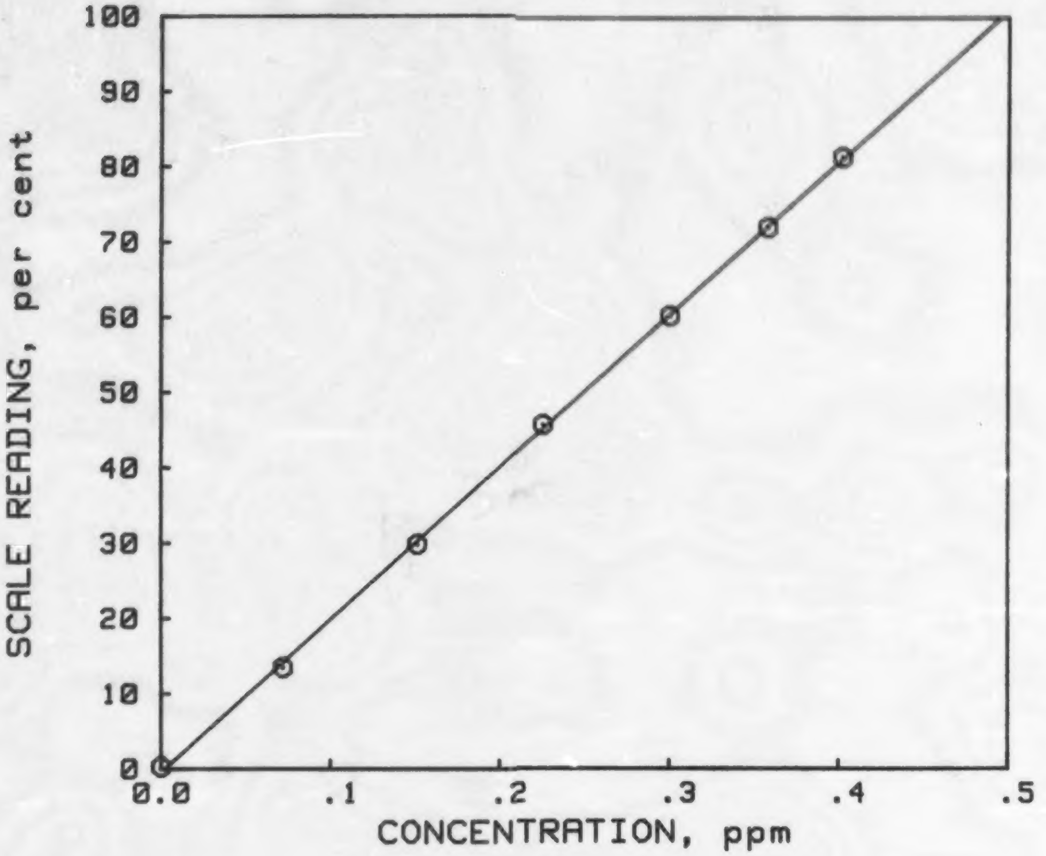
[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number 63.

[d] Average of absolute values.

[e] Data not required.



```
ANALYZER:   MONITOR LABS     Y = MX + A          DATA:  __X__      __Y__
MODEL:      8840
SERIAL No.: 63               M =  202.874          1    0.000        .232
POLLUTANT:  NO2               95% C.I.= ± 3.869    2     .072      13.486
RANGE:        .5 ppm                               3     .151      29.850
LOCATION:   DAMDF            A =      -.434        4     .225      45.760
DATE:       06/05/81                               5     .300      60.240
DATE CODE:   81.156           95% C.I.= ±  .990    6     .358      72.020
NAME:       RTI                                    7     .402      81.370
                             r =    .99986
```

Figure 38. Typical calibration curve for the Monitor Labs 8840 NO_2 response.

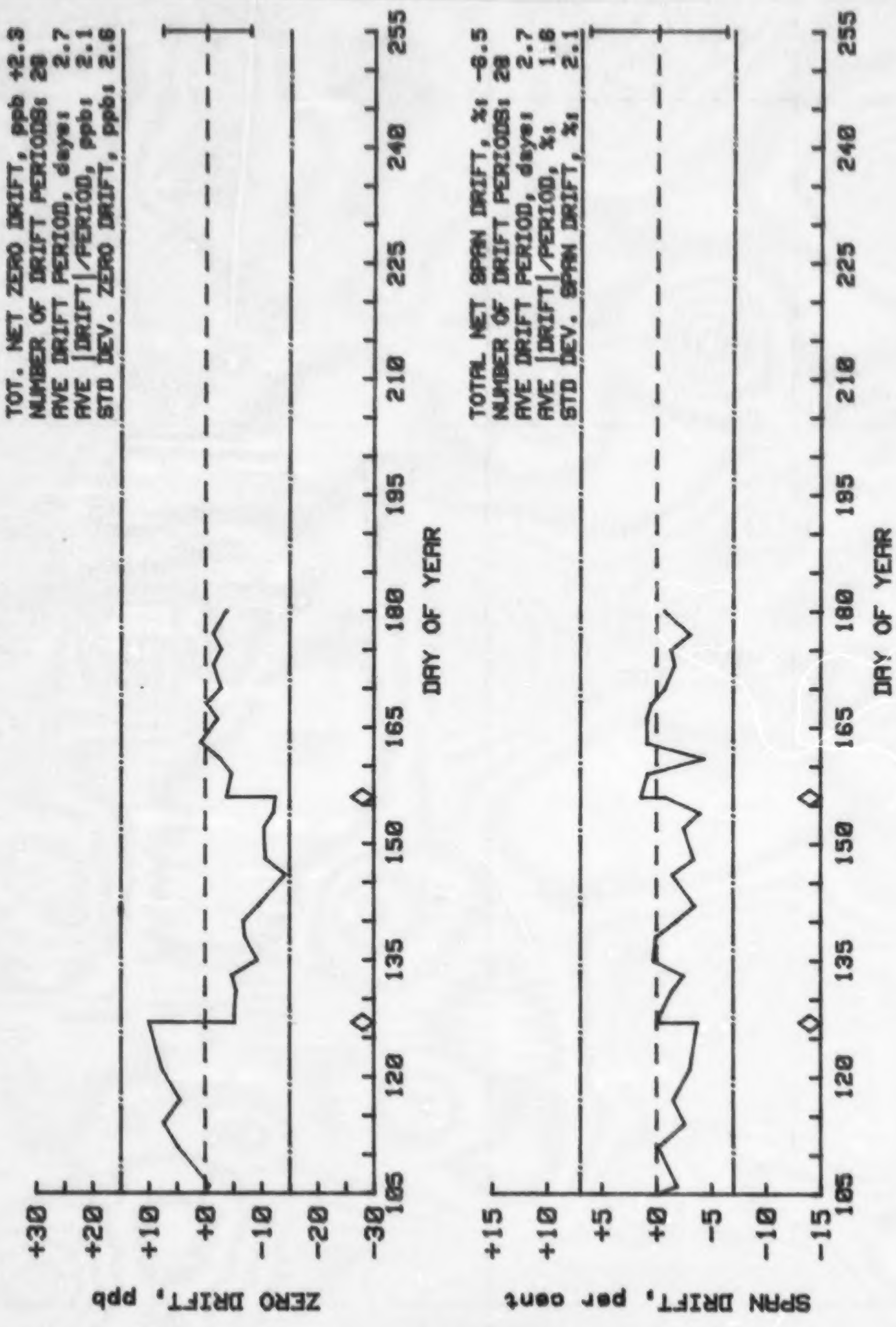


Figure 39. Zero and span drift in the Monitor Labs 8840 NO_2 readings during the Phase II ambient monitoring test.

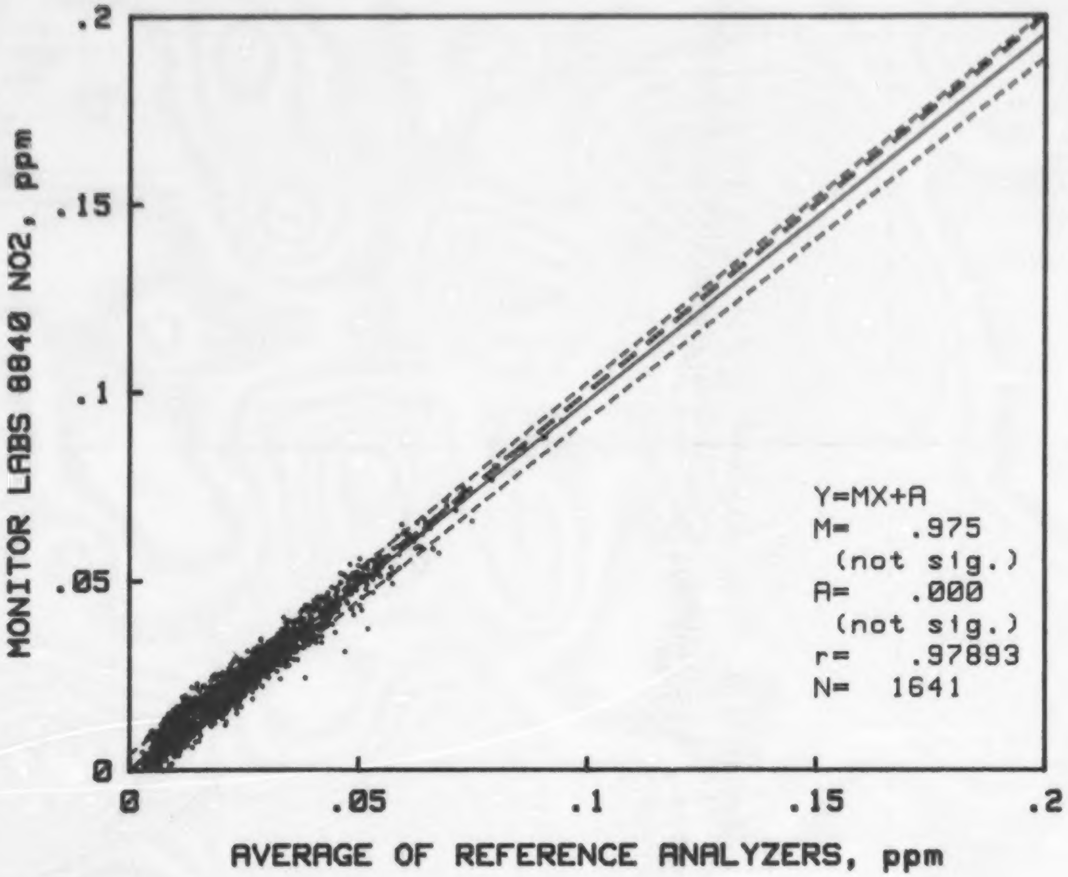
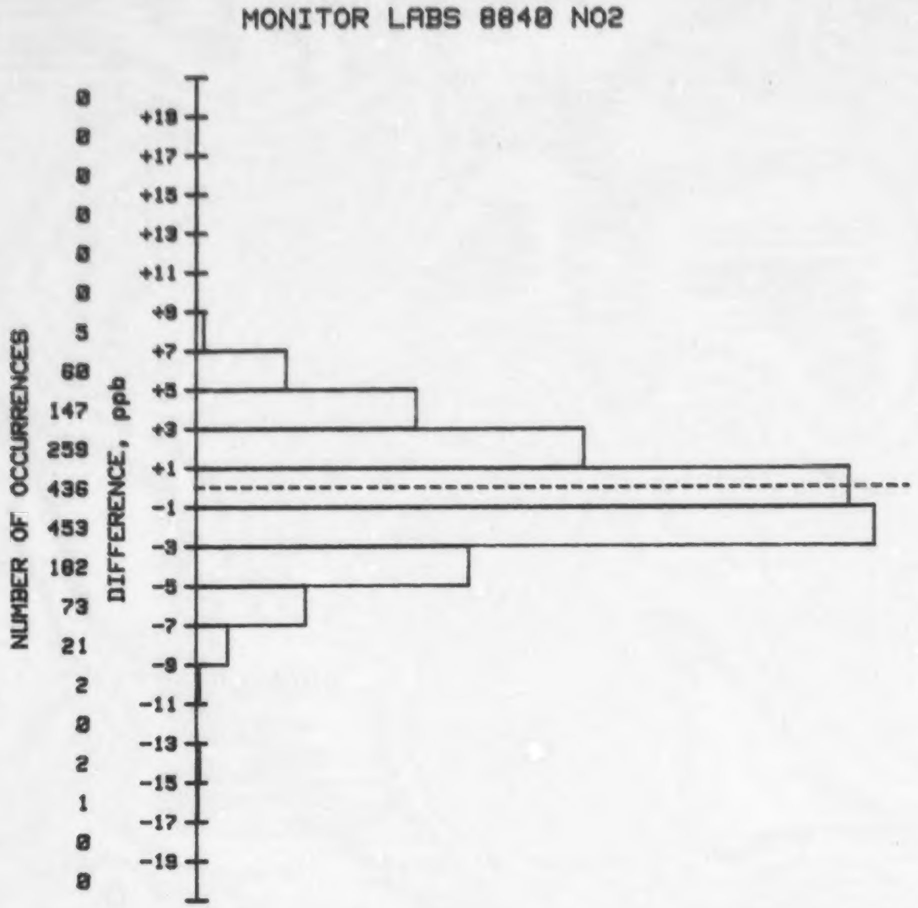


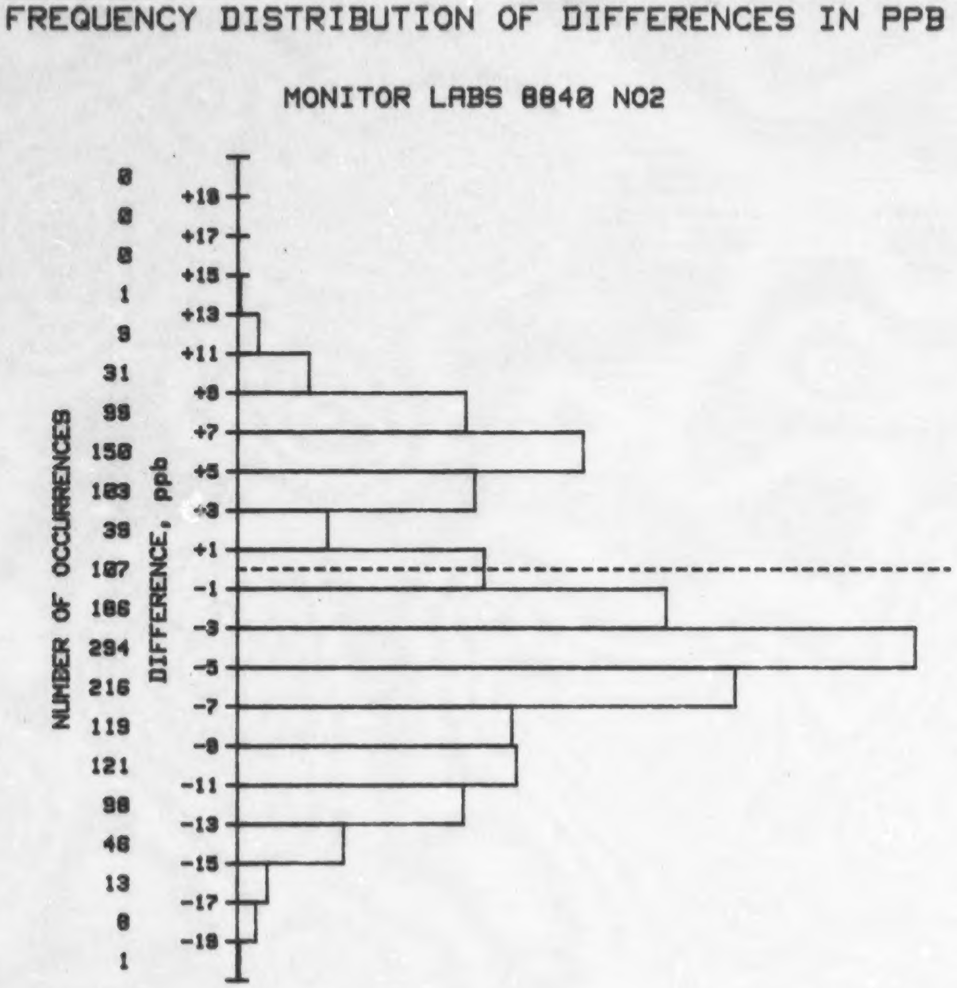
Figure 40. Correlation between the Monitor Labs 8840 and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB



TOTAL No. OF DATA PAIRS: 1641
CORRELATION COEFFICIENT: .978931
MEAN DIFFERENCE, ppb: -.48
STD. DEVIATION OF DIFFERENCES, ppb: 2.9749
MAX. ABSOLUTE DIFFERENCE, ppb: 16
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 41. Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.



TOTAL No. OF DATA PAIRS: 1641
CORRELATION COEFFICIENT: .919034
MEAN DIFFERENCE, ppb: -2.78
STD. DEVIATION OF DIFFERENCES, ppb: 6.4147
MAX. ABSOLUTE DIFFERENCE, ppb: 21
NO. ABSOLUTE DIFFERENCES >20: 1

Figure 42. Frequency distribution of differences in hourly NO_2 ambient air readings between the Monitor Labs 8440 and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Monitor Labs readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace ozone air drier bag	When required
Replace sample inlet filter	When required
Replace power fuse	Annually
Service vacuum pump	When required
Replace PMT assembly desiccant	Semiannually or when PMT assembly opened for repairs
Replace ozone filter bag	Every 3 months

Malfunctions

During Phase II testing in July 1981, the NO channel output signal abruptly began to drift erratically. Onsite service work by a factory representative revealed a defective thermoelectric cooler for the NO channel PMT. The cooler was replaced and the drift problem seemed to subside. However, 3 days after the replacement of the cooler, the drift problem returned. At this time the PMT cooler was functioning properly. Onsite investigation of the drift problem continued through August to the end of Phase II testing in September. Although the problem was never resolved, it is believed to be caused by failure of the PMT itself or something in the PMT circuitry. This failure resulted in the loss of data by this analyzer for 74 of the 150 days in this Phase II test.

General Comments

This analyzer utilizes the Monitor Labs prepackaged system of ozone-air desiccant and exhaust gas charcoal scrubbers. This system consists of permanently sealed plastic bags containing either Drierite® or activated charcoal. When the scrubbers are exhausted (1 to 3 weeks for the Drierite®), replacements must be purchased from Monitor Labs. The life of the Drierite® scrubber on this analyzer was extended for these tests by attaching a second refillable Drierite® scrubber to the inlet of the manufacturer-supplied scrubber. This effectively made the prepackaged scrubber a backup scrubber, subject to consumption only on exhaustion of the primary scrubber. Prior to incorporating this scrubber, careful tests were run to ensure that the additional scrubber caused no significant changes in flow characteristics within the ozone-air subsystem. None were observed.

PHILIPS PW 9762/02

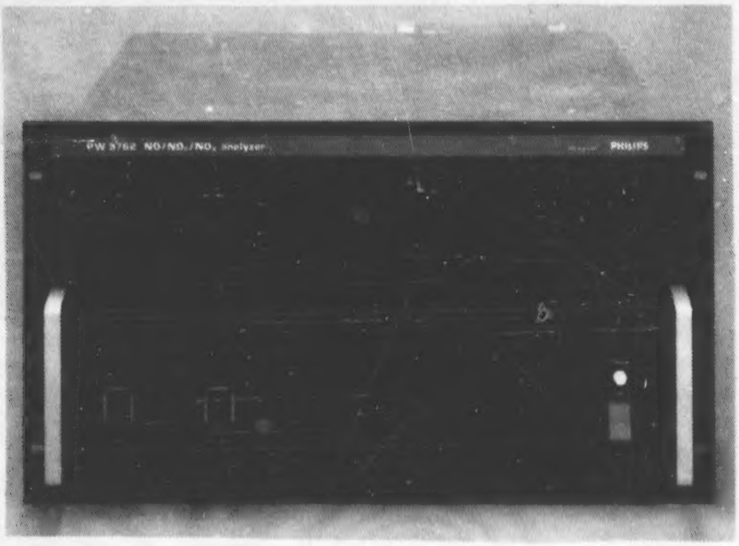


Figure 43. Philips Model PW 9762/02 NO/NO_2/NO_x Analyzer (RFNA-0879-040). Philips Electronics Instruments, Inc., 85 McKee Drive, Mahwah, NJ 07430.

General Description

The Philips Model PW 9762/02 NO/NO_2/NO_x Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with a single photomultiplier tube and reaction chamber. The input sample stream is alternately routed around and through the NO_2-to-NO converter to provide measurement of NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. A sample delay volume is provided so that more nearly identical air samples are analyzed during the NO_x and the NO portions of the cycle. In this way, possible negative NO_2 values from nonidentical input samples are avoided. In contrast to other analyzers of this type, the Model PW 9762/02 operates with a reaction chamber pressure near that of ambient. Increased quenching due to operation at near ambient pressures is compensated for by an increase in reaction chamber flow rate, a decrease in reaction chamber volume, and an increase in detection efficiency from a sensitive pulse counting detection technique. Another feature of this analyzer that contrasts with others is the use of a patented material that allows the converter to operate at the relatively low temperature of 110° C.

To be used as a reference analyzer, the Model PW 9762/02 must consist of the basic analyzer, the converter cartridge, and the sampler or PW 9731/20 dust filter. It must be operated on the 0 to 0.5 ppm range with or without any of the following options:

- Air sampler (manifold)
- Sample line heater
- Remote control set.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 10. Philips PW 9762/02 Laboratory Performance Test Results

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	
Noise – 80% URL	ppm	0.005	0.001	
Lower detectable limit	ppm	0.01	0.010	
Interferents	ppm			
SO_2		±0.02	<0.001	NO PHASE I TESTING ANTICIPATED
NO		±0.02	<-0.001	
NH_3		±0.02	0.000	
H_2O		±0.02	0.002	
Total interferents		≤0.04	0.002	
Zero drift – 12 h	ppm	±0.02	0.001	
Zero drift – 24 h	ppm	±0.02	0.001[d]	
Span drift – 20% URL	%	±20.0	1.67[d]	
Span drift – 80% URL	%	±5.0	1.29[d]	
Lag time	min	20	0.6	
Rise time	min	15	0.6	
Fall time	min	15	0.3	
Precision – 20% URL	ppm	0.020	0.001	
Precision – 80% URL	ppm	0.030	0.002	

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests.

[d] Average of absolute values.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace NO_2-to-NO converter	Every 3 months
Replace charcoal of Scrubber I (zero gas generator)	Every 3 months
Replace charcoal of Scrubber II (exhaust scrubber)	Every 3 months
Replace Drierite® in ozone air drier	Every 3 months
Service cooling fan	Every 3 months
Replace sample particulate filter	Every 3 months
Check pump pressure	Every 3 months
Perform leak test	Every 3 months
Check sample flow	Every 3 months
Clean pump silencer	Semiannually
Service vacuum pump	Annually

THERMO ELECTRON 14 B/E

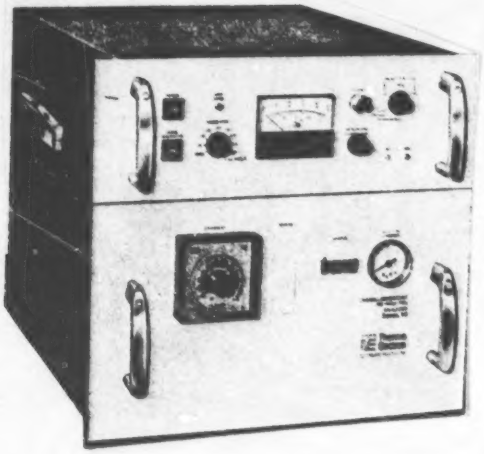


Figure 44. Thermo Electron Model 14 B/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer (RFNA-0179-035). Thermo Electron Corporation, Environmental Instruments Division, 108 South Street, Hopkinton, MA 01748.

General Description

The Thermo Electron Model 14 B/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2, as described in Appendix A. It is equipped with a single photomultiplier tube and reaction chamber. The input sample stream is alternately routed around the NO_2-to-NO converter and through the converter to provide measurement of NO and NO_x, respectively. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced within the analyzer by a high voltage discharge generator. Air for the ozone generator is dried within the analyzer by a permeation drier. Single zero and span controls are provided, affecting all three output channels collectively.

To be used as a reference method, the Model 14 B/E must be operated on the 0 to 0.5 ppm range with or without any of the following options:

- Teflon® particulate matter filter
- Voltage divider card
- Long-time signal integrator

- Indicating temperature controller
- Sample flowmeter
- Air filter

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 11. TECO 14 B/E Laboratory Perfromance Test Results

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	<0.001
Noise – 80% URL	ppm	0.005	0.001	NC
Lower detectable limit	ppm	0.01	0.011	0.010
Interferents	ppm			
SO_2		±0.02	<0.001	NC
NO		±0.02	-0.001	NC
NH_3		±0.02	0.010	<0.001
H_2O		±0.02	-0.010	0.004
Total interferents		<0.04	0.021	NC
Zero drift – 12 h	ppm	±0.02	<0.001	0.002
Zero drift – 24 h	ppm	±0.02	<0.001[d]	<0.001[d]
Span drift – 20% URL	%	±20.0	1.71[d]	NC
Span drift – 80% URL	%	±5.0	1.61[d]	NC
Lag time	min	20	0.4	0.4
Rise time	min	15	1.9	2.6
Fall time	min	15	2.4	2.9
Precision – 20% URL	ppm	0.020	<0.001	<0.001
Precision – 80% URL	ppm	0.030	0.001	0.001

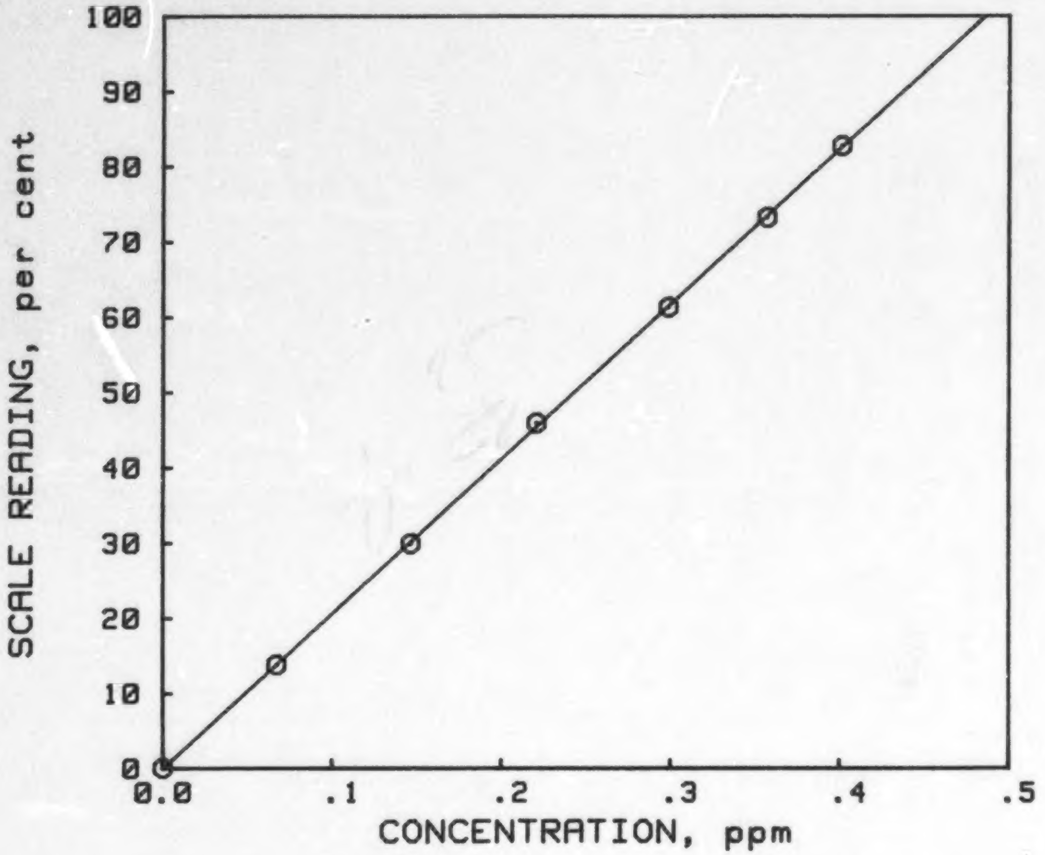
[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number AAM-0010.

[d] Average of absolute values.

NC = Testing of this parameter was not completed.



```
ANALYZER:    THERMO ELECTRON Y = MX + A         DATA:  __X__      __Y__
MODEL:       14 B/E
SERIAL No.:  AAM-0010                            1     0.000        .015
POLLUTANT:   NO2              M =   205.835      2      .067      13.807
RANGE:        .5 ppm           95% C.I.= ± 2.061 3      .146      29.899
LOCATION:    DAMDF                               4      .221      45.930
DATE:        06/05/81         A =        .000    5      .299      61.320
DATE CODE:    81.156           95% C.I.= ±  .524 6      .357      73.220
NAME:        RTI                                 7      .401      82.750
                              r =    .99996
```

Figure 45. Typical calibration curve for the Thermo Electron 14 B/E NO_2 response.

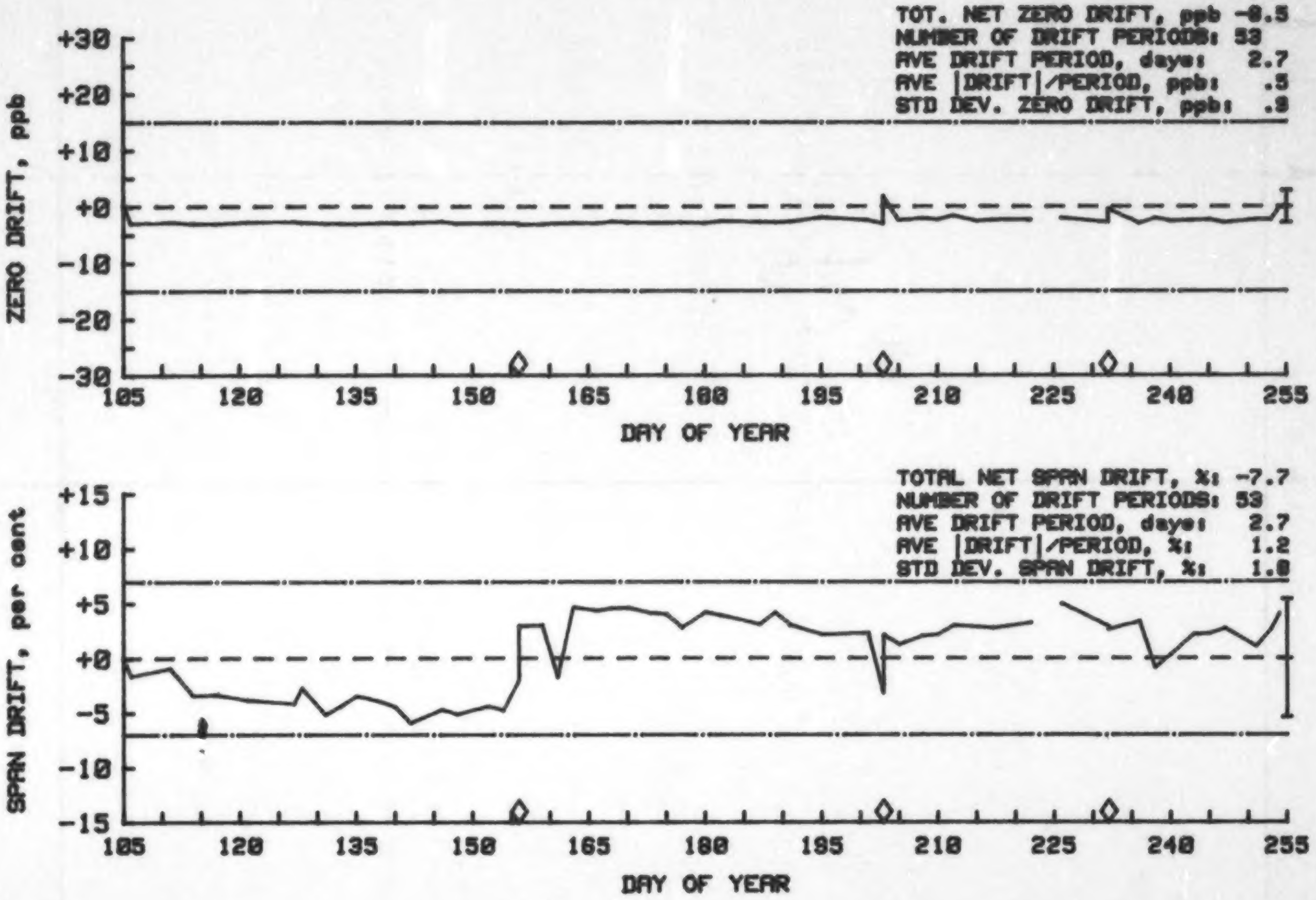


Figure 46. Zero and span drift in the Thermo Electron 14 B/E NO_2 readings during the Phase II ambient monitoring test.

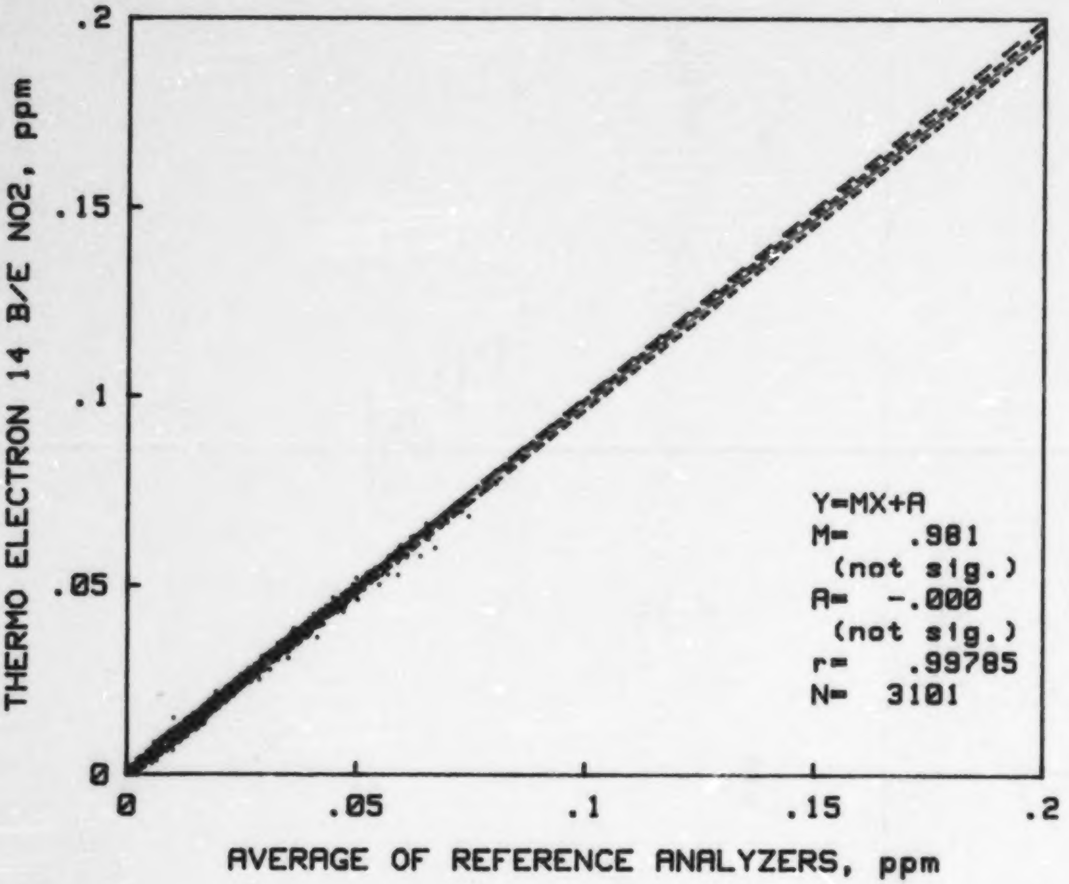
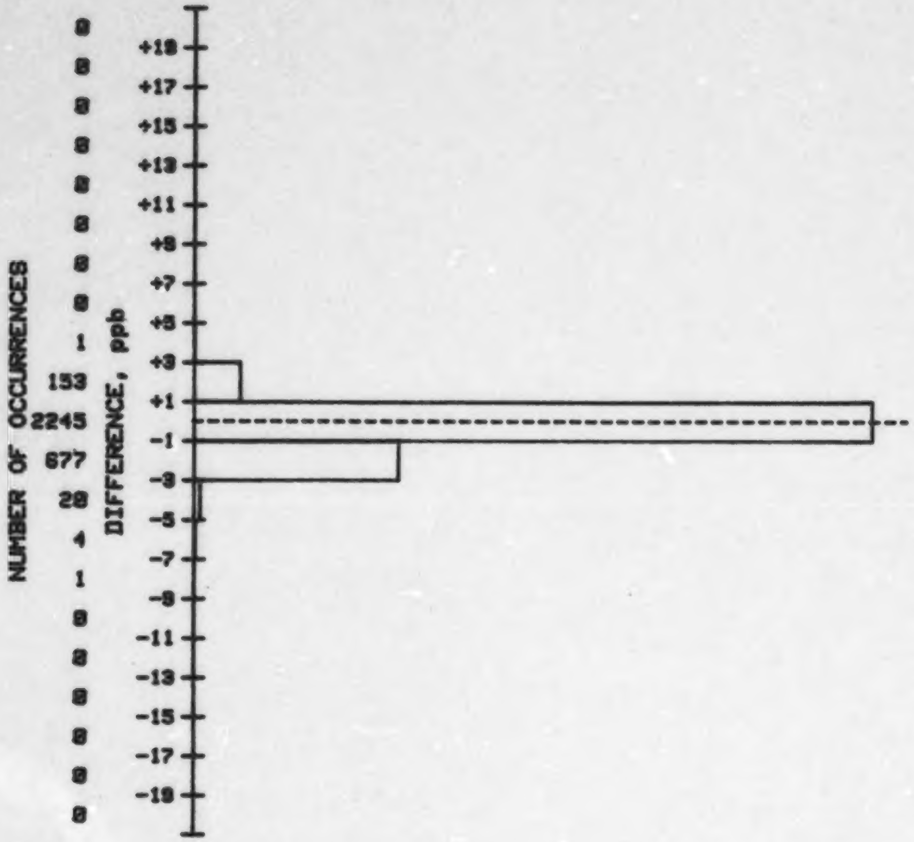


Figure 47. Correlation between the Thermo Electron 14 B/E and the average of the other analyzers during the Phase II ambient monitoring test.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

THERMO ELECTRON 14 B/E NO2

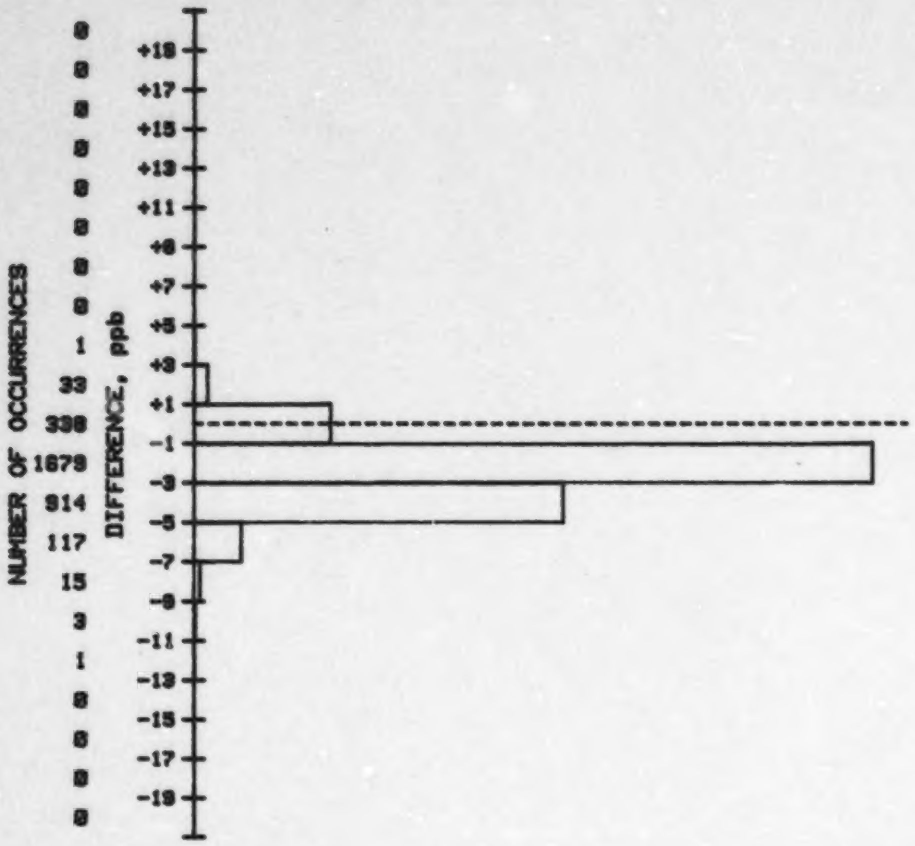


TOTAL No. OF DATA PAIRS:	3101
CORRELATION COEFFICIENT:	.997854
MEAN DIFFERENCE, ppb:	-.42
STD. DEVIATION OF DIFFERENCES, ppb:	.9010
MAX. ABSOLUTE DIFFERENCE, ppb:	7
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 48. Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 B/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

THERMO ELECTRON 14 B/E NO2



```
TOTAL No. OF DATA PAIRS:                    3101
CORRELATION COEFFICIENT:                        .993888
MEAN DIFFERENCE, ppb:                      -2.57
STD. DEVIATION OF DIFFERENCES, ppb:         1.4851
MAX. ABSOLUTE DIFFERENCE, ppb:             12
NO. ABSOLUTE DIFFERENCES >20:               0
```

Figure 49. Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 B/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Thermo Electron readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace ozone air drier	When required
Replace sample particulate filter	When required
Clean or replace flow capillaries	Every 3 months
Inspect and clean thermoelectric cooler fins	Semiannually
Recondition or replace NO_2-to-NO converter	When required

Malfunctions

The 14 B/E analyzer used in these tests had been purchased and used prior to designation of the model in January 1979. It was returned to the factory in June of 1979 for upgrading to designated status. It is reasonable to assume that this upgrading included installation of a new NO_2-to-NO converter, but we were unable to verify this assumption. Following the upgrading, the analyzer was not operated until commencement of the Phase I tests in May 1980.

On July 2, 1980, after 2 months of analyzer operation, the converter required replacement. As noted above, it is not clear if this was the total service time of the converter.

Operation of the new converter began with the converter temperature controller set at 375° C. Actual measurements of the converter temperature indicated that it was approximately 25° C below this setpoint. On July 10, the efficiency of the converter was determined to be approximately 70 percent, well below the EPA-specified minimum of 96 percent. Based on conversations with factory representatives, a decision was made to raise the temperature of the converter in an attempt to find an optimum operating point within the 96-percent specification. A 99.1-percent efficiency was achieved at a controller setting of 450° C (actual temperature 416° C). This setting is the maximum temperature controller setting recommended by the instrument manual.

On August 29 the efficiency was down to 91 percent. The temperature controller setting was raised to 475° C for 3 to 4 hours, then returned to 450° C. The efficiency returned to the 96- to 100-percent range. The efficiency, however, continued to fluctuate, requiring frequent temperature "shocks." TECO personnel recommended replacement, and a new converter was installed on October 1. The total operating time for the replaced converter was 3 months.

It is believed that the behavior of the converter replaced on October 2 (and possibly the previous one replaced July 2) was due to a defective batch of converter material obtained by TECO from their supplier. This belief seems to be supported by the fact that RTI personnel experienced similar behavior from the same type of converter in a TECO Model 14 D/E analyzer. This analyzer had successfully completed Phase I testing earlier in the year and was being used as a reference analyzer during subsequent tests. The converter material in the 14 D/E converter came from the same batch as that in the 14 B/E converter replaced on October 2. TECO personnel agreed with EPA that their quality control efforts concerning converter material should be increased. Converters filled from a subsequent batch of converter material operated satisfactorily in both the 14 B/E and the 14 D/E during Phase II testing from January to October 1981.

In August 1980, the 14 B/E failed three of four initial NO interferent equivalent tests with equivalent values of -0.0212, -0.0212, -0.0193, and -0.0207 ppm. The relevant atmosphere concentrations generated during the test were:

$[NO] = 0.0992$ ppm,

$[NO_2] = 0.500$ ppm, and

$[NO_x] = 0.599$ ppm.

After repair and adjustment of the analyzer electronics, the tests were repeated and passed.

This analyzer failed three of four 80-percent-of-scale (80 percent URL) drift tests in December 1980. The drift values actually observed during the test were -2.5, +9.0, -10.7, and +6.6 percent. These drifts seemed to be related to changes in analyzer line voltage rather than to changes in the temperature of the air surrounding the analyzer. TECO service personnel changed the Sola transformer, the ozone generator transformer, the PMT cooler assembly, and the analyzer power transformer. This service corrected the drift problem, and subsequent drift tests were passed.

General Comments

Phase I testing of this analyzer was attempted several times between May and December 1980. Because of repeated test failures by this analyzer, numerous component malfunctions, and various other test difficulties not related directly to this analyzer, some Phase I tests were never successfully completed. In January 1981 (after 7 months of testing attempts), EPA project personnel suspended the testing, postponing the completion of the test indefinitely because of overall postdesignation testing project time and budgetary constraints.

In December 1980, an attempt to conduct precision and drift testing was suspended due to an apparently insufficient NO_2 range. The problem was traced to an over-range condition in the NO_x operational amplifier, which was causing a depressed response in the NO_2 channel. Gas phase titration (GPT) was being used as the atmosphere generation technique for these tests. The GPT was set up to produce appropriate concentration levels of NO and NO_2 at the A_{20} concentration level. Dilution air was then reduced to produce the A_{80} concentration levels. Because of this method of generation, the A_{80} NO_2 concentration was 0.42 ppm while the NO concentration was 0.28 ppm, producing a NO_x concentration of 0.70 ppm or ~140 percent of the 0.5-ppm scale. This level of NO_x caused saturation of the NO_x amplifier and subsequent depression of the NO_2 signal. Additional tests indicated that the saturation point for the amplifiers used in this analyzer was 120 to 125 percent of full scale (i.e., 0.60 to 0.65 ppm). This is somewhat lower than might be anticipated, since amplifiers used in analogous applications are typically chosen to be capable of overranging as much as 100 percent of full scale.

Simple recomputation of the GPT parameters permitted successful completion of this test. However, users should be aware of the limited overranging capability of this analyzer in monitoring situations where NO_x concentrations may exceed 0.60 to 0.65 ppm and the 0 to 0.5 ppm analyzer range is being employed (all three output channels are constrained to the same range).

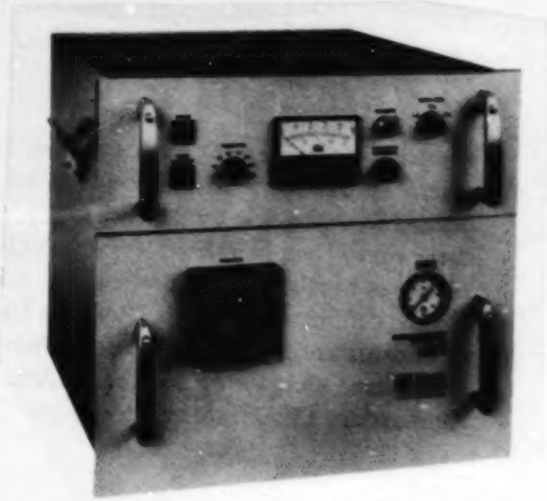


Figure 50. Thermo Electron Model 14 D/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer (RFNA-0279-037). Thermo Electron Corporation, Environmental Instruments Division, 108 South Street, Hopkinton, MA 01748.

General Description

The Thermo Electron Model 14 D/E Chemiluminescent $NO/NO_2/NO_x$ Analyzer operates on the principle of gas phase chemiluminescence based on the reaction of NO and O_3 to form NO_2 as described in Appendix A. It is equipped with a single photomultiplier tube, but has dual reaction chambers. The input sample stream is split, with one-half directed to one reaction chamber where the NO is measured and the other half directed through the NO_2-to-NO converter to the other reaction chamber where NO_x is measured. Utilizing a mechanical chopper, the PMT is exposed alternately to the NO reaction chamber and the NO_x reaction chamber. The NO signal is electronically subtracted from the NO_x signal to produce the NO_2 signal. The ozone required for the analysis is produced by a high voltage discharge generator. Single zero and span controls are provided affecting all three output channels collectively.

To be used as a reference analyzer, the Model 14 D/E must be operated on the 0 to 0.5 ppm range with or without any of the following options:

- Teflon® particulate matter filter
- Voltage divider card.

Ambient air surrounding the analyzer must be within the range of 20° to 30° C, inclusive, and line voltage to the analyzer must be within the range of 105 to 125 Vac, inclusive.

Table 12. TECO 14 D/E Laboratory Performance Test Results

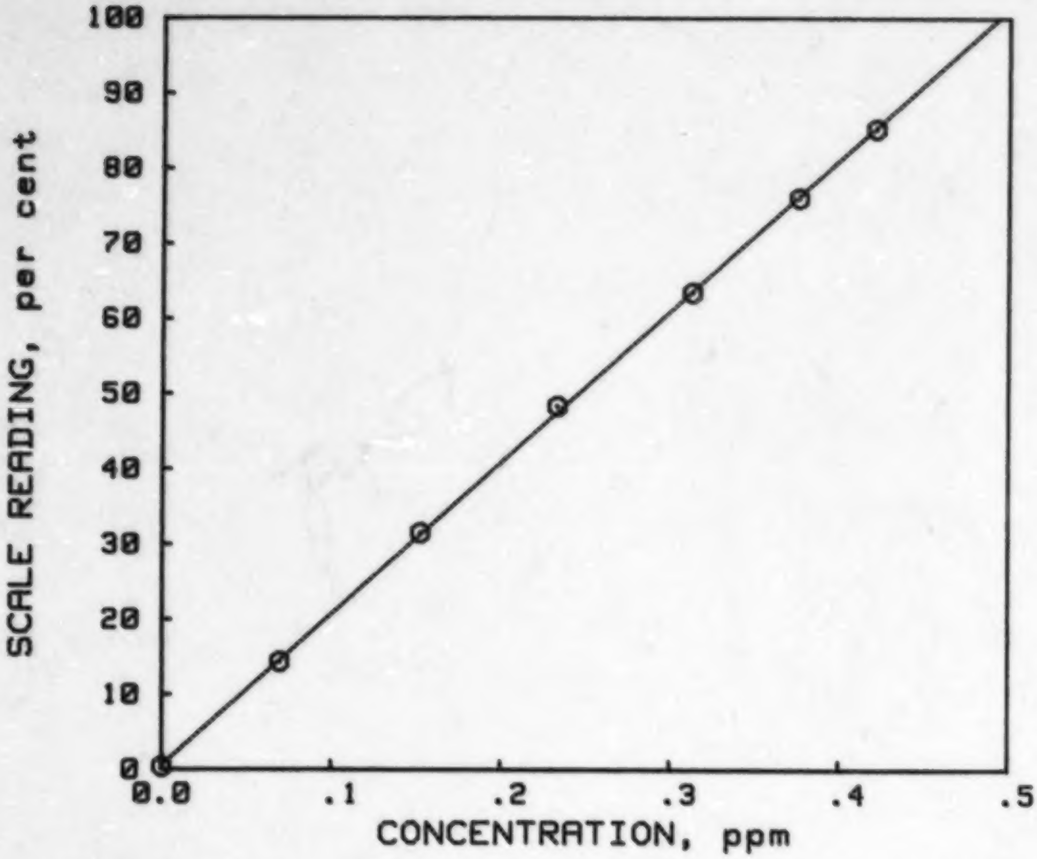
Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	EPA test results[c]
Noise – 0% URL	ppm	0.005	<0.001	0.002
Noise – 80% URL	ppm	0.005	0.001	0.002
Lower detectable limit	ppm	0.01	0.011	0.009
Interferents	ppm			
SO_2		±0.02	0.001	0.001
NO		±0.02	0.001	0.009
NH_3		±0.02	0.009	-0.001
H_2O		±0.02	-0.007	-0.002
Total interferents		<0.04	0.022	0.012
Zero drift – 12 h	ppm	±0.02	0.001	0.004
Zero drift – 24 h	ppm	±0.02	0.002[d]	0.003[d]
Span drift – 20% URL	%	±20.0	2.04[d]	5.64[d]
Span drift – 80% URL	%	±5.0	1.56[d]	1.39[d]
Lag time	min	20	<0.1	1.0
Rise time	min	15	4.4	3.8
Fall time	min	15	5.1	1.0
Precision – 20% URL	ppm	0.020	0.001	0.005
Precision – 80% URL	ppm	0.030	0.001	0.004

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from EPA Phase I postdesignation tests, serial number ADM/E-8788-102.

[d] Average of absolute values.



```
ANALYZER:    THERMO ELECTRON Y = MX + A        DATA:  __X__      __Y__
MODEL:       14 D/E
SERIAL No.:  ADM/E-0700-102  M =  201.561         1   0.000         .289
POLLUTANT:   NO2              95% C.I.= ± 2.946   2    .069       14.335
RANGE:        .5 ppm                              3    .153       31.507
LOCATION:    DAMDF                                4    .233       48.400
DATE:        06/05/81        A =       .557       5    .313       63.470
DATE CODE:    81.156          95% C.I.= ±  .787   6    .376       76.040
NAME:        RTI                                  7    .421       85.260
                             r =    .99992
```

Figure 51. Typical calibration curve for the Thermo Electron 14 D/E NO_2 response.

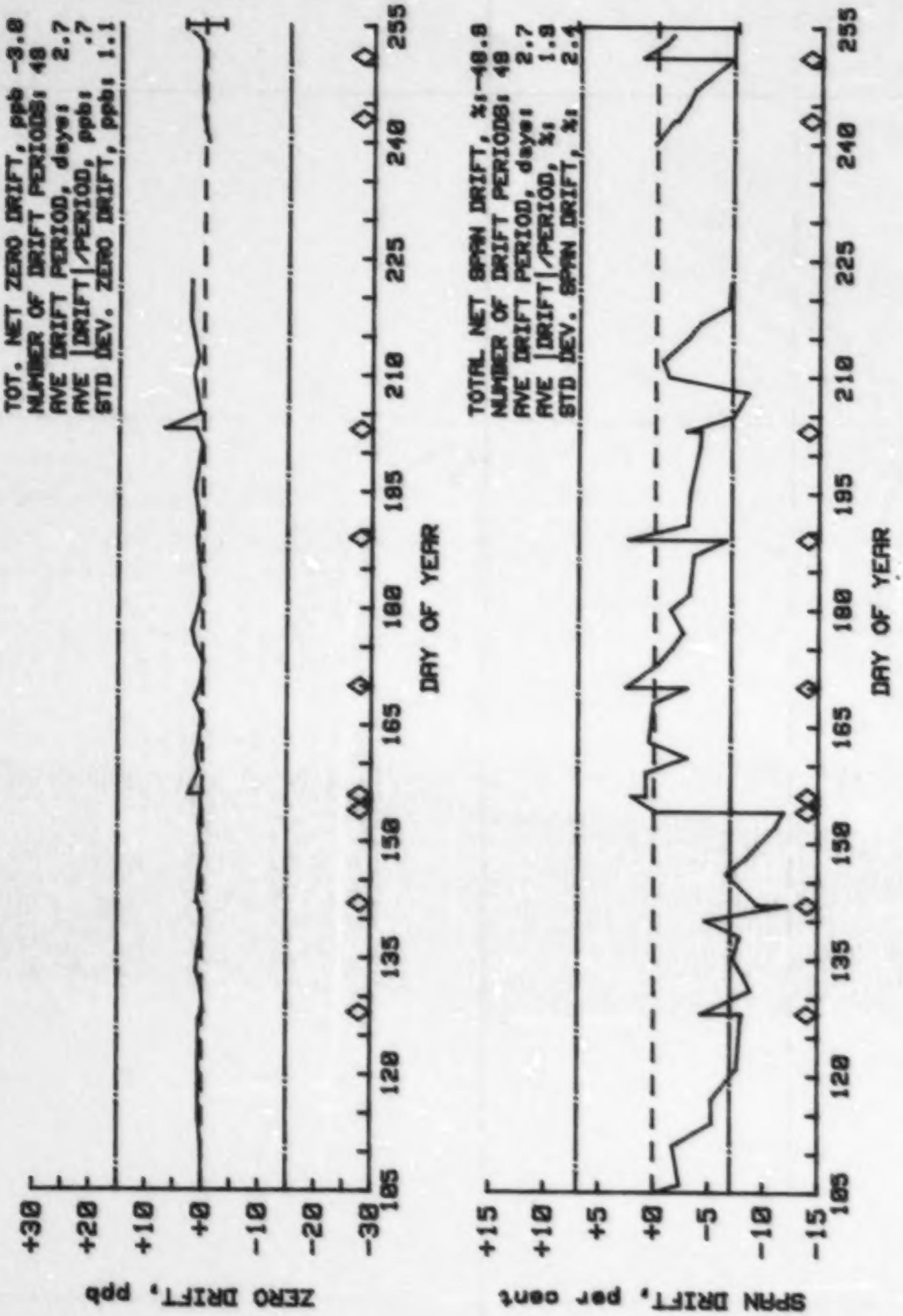


Figure 52. Zero and span drift in the Thermo Electron 14 D/E NO_2 reading during the Phase II ambient monitoring test.

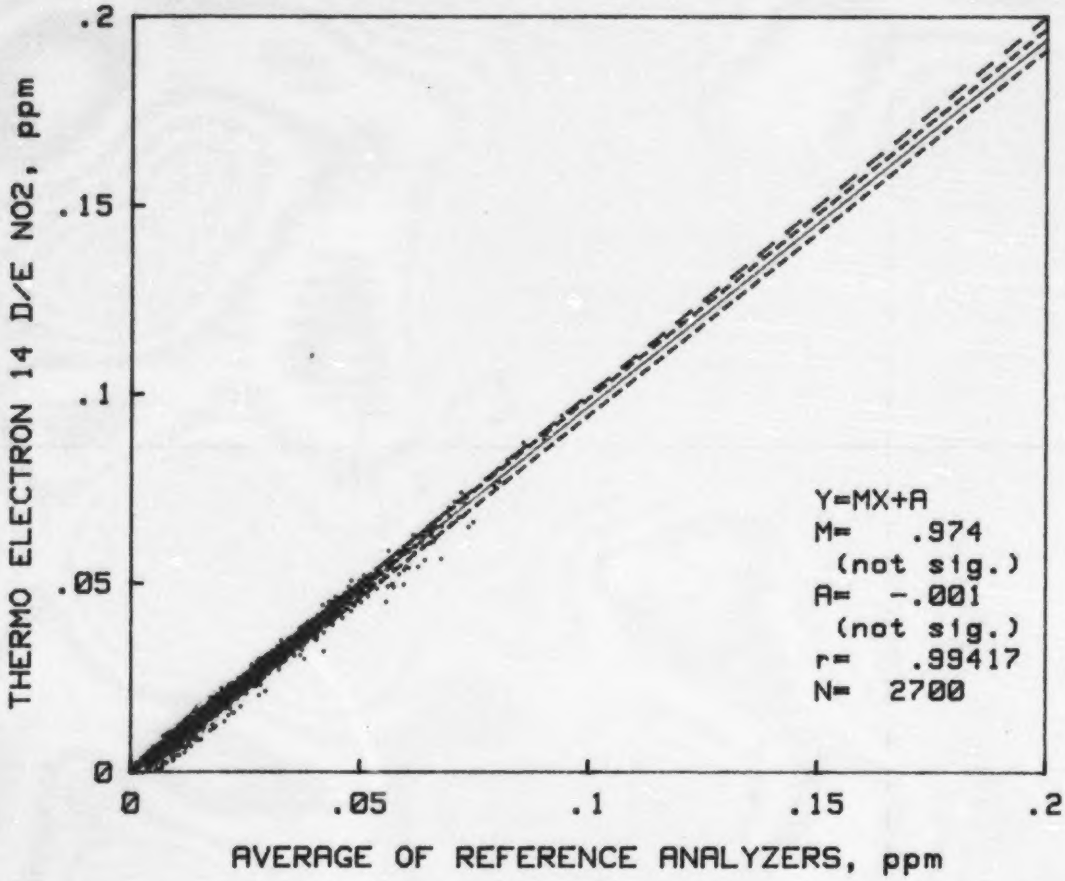
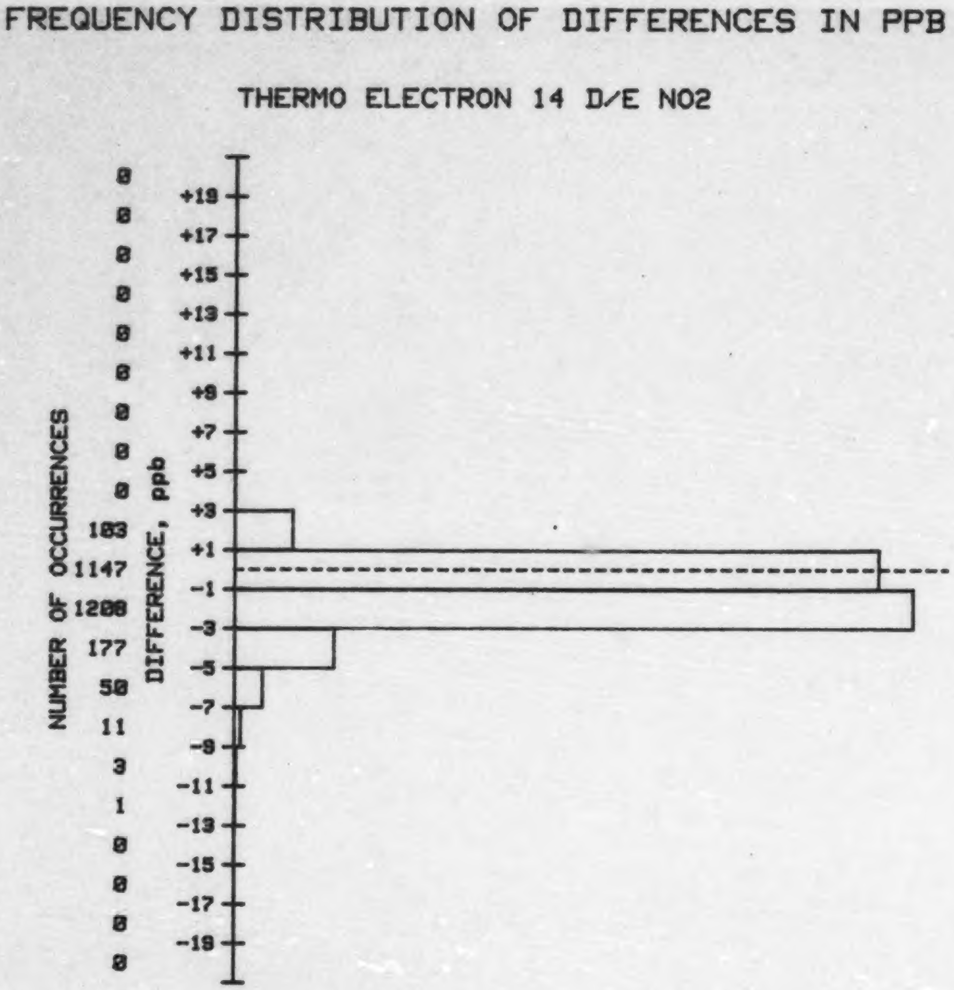


Figure 53. Correlation between the Thermo Electron 14 D/E and the average of the other analyzers during the Phase II ambient monitoring test.

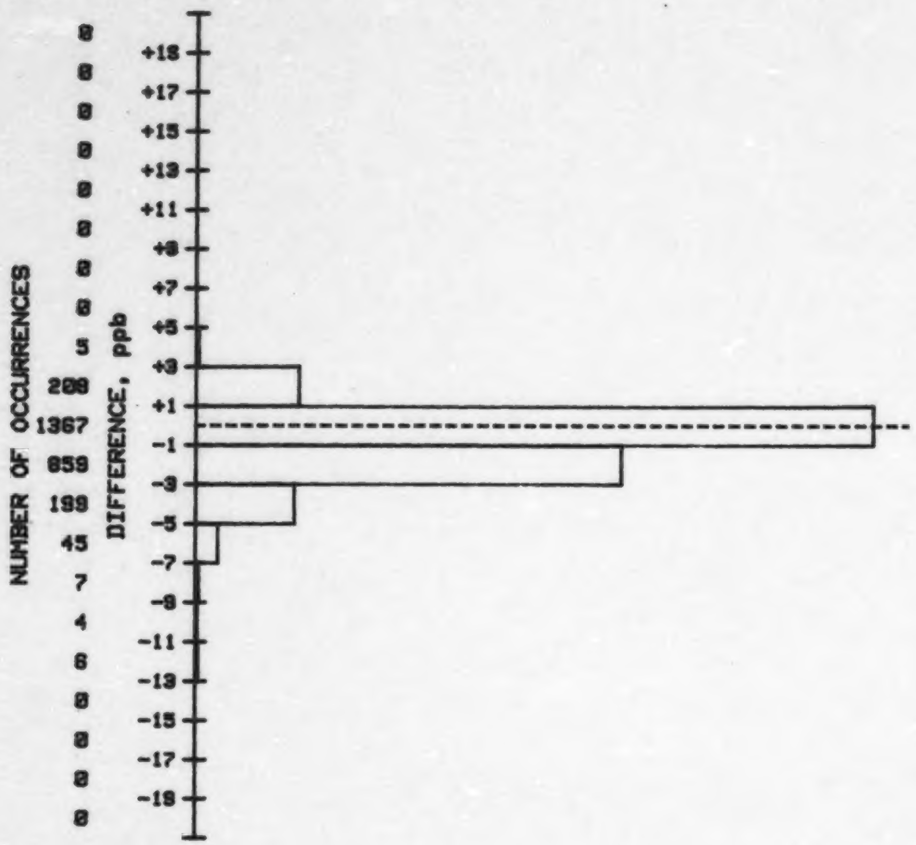


TOTAL No. OF DATA PAIRS: 2700
CORRELATION COEFFICIENT: .994171
MEAN DIFFERENCE, ppb: -1.25
STD. DEVIATION OF DIFFERENCES, ppb: 1.4708
MAX. ABSOLUTE DIFFERENCE, ppb: 11
NO. ABSOLUTE DIFFERENCES >20: 0

Figure 54. Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 D/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. All readings corrected for zero and span drift.

FREQUENCY DISTRIBUTION OF DIFFERENCES IN PPB

THERMO ELECTRON 14 D/E NO2



TOTAL No. OF DATA PAIRS:	2700
CORRELATION COEFFICIENT:	.993185
MEAN DIFFERENCE, ppb:	-.94
STD. DEVIATION OF DIFFERENCES, ppb:	1.6918
MAX. ABSOLUTE DIFFERENCE, ppb:	13
NO. ABSOLUTE DIFFERENCES >20:	0

Figure 55. Frequency distribution of differences in hourly NO_2 ambient air readings between the Thermo Electron 14 D/E and the average of simultaneous readings from the other analyzers during the Phase II ambient monitoring test. Thermo Electron readings not corrected for zero and span drift.

Manufacturer's Recommended Maintenance

Operation	Frequency
Replace ozone air drier	When required
Replace sample particulate filter	When required
Clean or replace flow capillaries	Every 3 months
Inspect and clean thermoelectric cooler fins	Semiannually
Clean photodiode pickups	Semiannually
Recondition or replace NO_2-to-NO converter	Annually or when required

Malfunctions

During the period of Phase I and Phase II testing (February 1980 to September 1981), the NO_2-to-NO converter failed and was replaced two times. The first replacement took place in December 1980 after the converter had been in service for approximately 8 months. The second replacement was in August 1981. This converter had been in service for 5 months. The third converter had been in service for approximately 1 month when Phase II testing was completed and the analyzer was deactivated.

General Comments

Because the NO_2 signal is produced by electronically subtracting the NO signal from the NO_x signal, a balance must exist between the NO and the NO_x channels. When the NO concentration is equal to the NO_x concentration, both channels should read the same, otherwise all NO_2 readings will be erroneous. In this analyzer, the sample stream is drawn into the analyzer through a capillary and is then split into two streams, one analyzed for NO and the other analyzed for NO_x. The NO_x sample stream goes through the NO_2-to-NO converter, while the NO stream goes through a flow metering valve that stimulates the pressure drop across the converter in the NO_x channel. The electronic span of the single signal amplifier is adjusted by a span pot on the front panel of the instrument while the analyzer is measuring NO_x. The NO response is then adjusted by matching the signal from the NO channel with that from the NO_x channel by adjusting the amount of NO sample flow with the flow metering valve. Because the total sample flow is fixed by the sample capillary, any flow adjustment made in the NO sample stream also affects the NO_x flow, which affects the NO_x response. Adjusting the NO_x span pot, in turn, affects the NO response. Thus, a delicate balance must be achieved between the NO_x span pot and the NO flow metering valve to balance the signals from the NO and NO_x channels. Although experience showed this adjustment to be necessary only once a month, it is a tedious and time-consuming process.

During Phase II testing, routine zero/span operations for all nine analyzers in the test were conducted simultaneously two or three times per week. During each span operation, the NO_2 span atmosphere was generated by gas phase titration of NO with O_3. The concentration of that atmosphere was determined independently for each analyzer based on the residual NO detected in the span matrix by the analyzer's previously calibrated NO channel. Throughout the test, this analyzer consistently analyzed the NO remaining in the span matrix as being 0.014 ppm less than the average detected by the eight other analyzers (actual average: 0.0139 with a standard deviation of 0.0013 ppm). This discrepancy is significant since the variation in NO concentration detected by the other analyzers averaged 0.0039 ppm with a standard deviation of 0.0016 ppm. The actual cause of this phenomenon has not been determined. One possible explanation is a memory effect in the single photomultiplier tube.

APPENDIX A

MEASUREMENT PRINCIPLE FOR NITROGEN DIOXIDE ANALYZERS

All nitrogen dioxide analyzers designated by EPA to date are reference methods and, accordingly, employ the measurement principle specified in Appendix F of 40 CFR Part 50, "Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescence)." This principle is described in this appendix to enhance the reader's understanding of the analyzers.

The quantification of nitrogen dioxide by this principle depends on the photometric detection of the chemiluminescence (chemically produced light) produced by the gas-phase reaction of nitric oxide (NO) and ozone (O_3) to form nitrogen dioxide (NO_2) and oxygen (O_2). In this reaction, best described by the equations

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad (1)$$

and

$$NO_2^* \rightarrow NO_2 + h\nu \, , \qquad (2)$$

one molecule of NO reacts with one molecule of O_3 to produce one molecule of NO_2. This NO_2 is formed in an electronically excited state, as signified by the star in equation (1). It immediately reverts to its electronic ground state, releasing its extra energy as a photon of light, represented as $h\nu$ in equation (2). The light produced by the reaction ranges in wavelength from about 600 to about 3,000 nanometers and has a maximum intensity at about 1,100 namometers. As can be seen from equations (1) and (2), there is a 1:1 correspondence between the number of molecules of NO entering the reaction and the number of photons of light produced. Therefore, in the presence of excess ozone, the intensity of the light produced by the reaction is directly proportional to the amount of NO input.

NO_2 does not react with O_3 to produce chemiluminescence; thus, it cannot be directly detected in this manner. However, NO_2 can be reduced to NO with the aid of hot molybdenum, carbon, or various other reducing agents. The reduction of the NO_2 proceeds according to the equation:

$$NO_2 + X \rightarrow NO + XO \qquad (3)$$

where X is the reducing agent and XO is the oxide of that agent. Again, there is a 1:1 correspondence in the reaction, this time between the NO_2 entering the reaction and the NO formed. This NO may be detected photometrically by reaction with O_3 as described above, thus providing an indirect detection of NO_2 by the chemiluminescence reaction.

The EPA measurement principle quantifies two species within the ambient sample, NO and NO_x, to provide an indirect measure of the NO_2 present. NO is quantified as described above by reacting the unaltered ambient sample with O_3 and measuring the intensity of the light produced. NO_x is not an actual compound that exists within the sample, but rather symbolizes an artificial quantity termed "oxides of nitrogen." NO_x is defined as the sum of NO, NO_2, and any other oxides of nitrogen (e.g., N_2O, N_2O_4, etc.) existing within the sample. In reality, the amount of all oxides of nitrogen other than NO and NO_2 in ambient air is quite small. Therefore, NO_x can be defined in essence as being the sum of NO and NO_2 as represented by the equation:

$$NO_x = NO + NO_2 \quad . \tag{4}$$

NO_x is determined by passing the ambient sample through a hot reducing agent, which converts any NO_2 present to NO. The reducing agent is contained in the NO_2-to-NO converter. This newly formed NO plus any NO originally present in the sample is reacted with O_3, and the intensity of the light produced is measured. The difference between the light intensity produced during reaction of NO_x and that produced during reaction of NO is proportional to the amount of NO_2 in the original sample.

Currently designated analyzers measure NO_2 by using one of two basic configurations. In the single-chamber or cyclic design, NO and O_3 are combined in a single reaction chamber, which is continuously monitored by a single photomultiplier tube (PMT). The PMT converts the light energy produced by the reaction of NO and O_3 into electrical energy, which is processed into a current or voltage proportional to the light energy produced. A valve in the sample flow path alternately routes the incoming sample around and through the NO_2-to-NO converter, thus providing alternating quantitation of NO and NO_x, respectively. The electrical signal produced during each half of the valve cycle is stored in sample-and-hold amplifiers. At the end of each half-cycle, the signal value of the NO sample-and-hold amplifier is subtracted electronically from the signal value of the corresponding NO_x amplifier. The difference is then presented as the level of NO_2 in the sample.

In the dual-chamber design, two separate reaction chambers are provided--one for NO and one for NO_x. These chambers may be monitored by a single PMT, alternately viewing each chamber at a frequency of 35 to 75 Hz, or the chambers may be monitored by two separate PMTs, one dedicated to each chamber. The incoming sample is split, with one-half going directly to one chamber for quantitation of NO. The other half of the sample is routed to the second chamber after first being passed through the NO_2-to-NO converter, thus providing quantitation of NO_x. The signals produced from the NO and NO_x channels are continuously subtracted electronically, providing a real-time measure of NO_2 concentration.

Each design has various advantages. Dual-chamber analyzers measure NO and NO_x simultaneously and continuously to provide a continuous measurement of NO_2. But the two channels require careful pneumatic and electronic balancing and contain additional parts that may add to the cost, size, and complexity of the analyzer. Single-chamber analyzers are simpler and easier to balance, but have a cyclic operation that requires a valve that must operate hundreds of times per day. Also, the nonsimultaneous measurement of NO and NO_x means that the derived NO_2 measurement may be subject to error if the NO or NO_x concentrations change during the cycle.

Much discussion has arisen concerning whether or not cyclic analyzers introduce a bias (either positive or negative) into the NO_2 determination, particularly during periods of rapid fluctuation of ambient NO and NO_2 levels. In currently designated analyzers employing the single-chamber design, the valve cycle time varies between 15 and 60 seconds. Thus, updated NO_2 concentrations are reported at least once every 30 seconds. Additionally, ambient air levels of NO and NO_2 generally fluctuate gradually at properly sited monitoring stations. Based on cycle times of no more than 60 seconds and the average rate of ambient NO and NO_2 fluctuation, EPA believes that the cyclic analyzers do not perform significantly differently from noncyclic ones with respect to bias introduced into the NO_2 levels. This is particularly true when one considers the fact that most ambient data are based on hourly averages. In this situation the hourly integration period serves to average out random biases that may exist on a moment-to-moment basis. However, users should be aware that if cyclic analyzers are used to monitor atmospheres characterized by rapidly fluctuating NO and NO_2 concentrations, which tend to follow long-term trends, some bias could develop in the NO_2 measurement.

Since the reaction with NO requires O_3, and since O_3 is an unstable compound that cannot be stored, analyzers utilizing this principle must be capable of producing a continuous, real-time supply of O_3. This is usually accomplished by passing air through a device termed an ozone generator. However, one currently designated analyzer may be configured to pass pure oxygen through the generator. The generator usually utilizes a high voltage discharge to ionize the air and produce ozone, although irradiation by ultraviolet light may also be used. In those cases where high voltage discharge is used as the generation technique and air is used as the source gas, it is absolutely essential that the air be dry (i.e., dewpoint <-20° C). This is necessary because, in the presence of water vapor, a high voltage discharge is capable of forming nitric acid by association of the oxygen and nitrogen in the air. This nitric acid is extremely corrosive and can damage components of the generator and the reaction chamber(s). Most currently designated analyzers employ an external scrubber containing Drierite® or some similar desiccant as the drying agent. One analyzer, however, utilizes an internal permeation dryer to dry the source air. When ultraviolet irradiation is utilized for O_3 generation, the source gas must also be free of organic compounds (e.g., olefins, aldehydes, ketones, and alcohols) that consume ozone, thus reducing the efficiency of the generation process. High voltage discharge generators are capable of generating such high concentrations of ozone that depletion by organic compounds in the source matrix does not pose a problem.

As was stated earlier, this measurement principle and its accompanying calibration procedure are formally documented in Appendix F of 40 CFR Part 50. Further explanation of the measurement principle and particularly the associated calibration procedure is presented in the EPA document "Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide" (EPA-600/4-75-003) by E. C. Ellis. This document is available through the National Technical Information Service, Springfield, Virginia 22161.